COMBUSTION

AND

FLAME

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VOLUME II

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COMBUSTION & FLAME

Quarterly Journal of The Combustion Institute

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BUTTERWORTHS SCIENTIFIC PUBLICATIONS

COMBUSTION & FLAME

Quarterly Journal of The Combustion Institute

Editorial

The first year of a new journal is seldom wholly predictable. Even when the specialist field is fairly well defined, as is the case for *Combustion and Flame*, the advantages of bringing all this work into a single journal have always to be weighed against the disadvantages of still further splitting of the field of broad publications on Physical Chemistry. Workers active in the subject have to decide whether to abandon old habits of publication in scattered journals, often with a series of articles already printed, in order to take advantage of the much closer scientific interaction with related researches, when all are brought together in a specialist journal. Libraries have to assess whether the addition of yet another journal to their shelves and their budgets is warranted by the demands of their readers.

For *Combustion and Flame* some of these problems encountered by any new specialist journal are made much less unsettled by the sponsorship of the Combustion Institute. This provides various links between scientists interested in combustion generally, and the Journal forms an additional link.

There is already satisfactory evidence that this specialist Journal has proved a worth while newcomer to scientific literature. As was stated at its inception, *Combustion and Flame* grew out of and now forms a parallel to the journal *Fuel* which still continues, but no longer publishes papers on combustion. The new Journal became an official publication of the Combustion Institute. During the first year, some 38 papers dealing with original work have appeared in *Combustion and Flame*. The majority of these have dealt with the non-equilibrium conditions characteristic of flames generally. These involve concentrations of free radicals, atoms and ions which are often high relative to thermodynamic equilibrium at the same translational temperature. There have been only a few papers on the reaction kinetics and reaction mechanism of the slow combustion processes preceding flames. This is in part to be expected, since the physical chemistry of such 'low temperature' reactions often bears quite as close a relationship to general reaction kinetics as to flames. On the other hand, hydrodynamic aspects of combustion, as in turbulent flames and in the region of detonation, belong much more completely to the field it is aimed to cover in the present Journal. More publications may be expected to appear in our pages as more authors come to realize this.

In addition to publishing original theoretical and experimental work on combustion and flame the Journal aims to sponsor somewhat longer review articles from time to time, where there are suitable domains awaiting treatment. Normally such review articles are requested by the Editors, but plans or proposals for review articles would be welcome from authors interested in their preparation. News items also form a useful feature

especially for members of the Combustion Institute who might otherwise lose touch. Here again the collaboration of readers is invited.

In connection with the Combustion Symposium that is to be held in London and Oxford in 1958, it is anticipated that not all the papers submitted can be taken into the Symposium Programme itself. Papers on other topics, provided their nature conforms with the general programme of *Combustion and Flame*, will be considered for publication in that Journal as early as possible.

In all, the first year of publication has brought together a range of activities related to combustion in a way that may be fairly regarded as giving promise of healthy continuance and growth. It seems appropriate to put on record good wishes for much further service by this Journal to a very ancient but still very lively branch of science.

The Ignition of Combustible Gases by Flames

H. G. WOLFHARD and D. S. BURGESS

The ignition of a stoichiometric methane–nitric oxide mixture by stationary pilot flames has been investigated. These pilot flames can be burned indefinitely in the surrounding explosive mixture without causing ignition if the temperature or mass flow of the pilot is insufficient. For very small pilot flames the condition for ignition is a minimum energy flow (cal/s), whereas for large pilots a minimum temperature is necessary. This minimum ignition temperature is little related to the spontaneous ignition temperature. Ignition does not occur close to the burning zone of the pilot, but at the end of a luminous reacting column in which reaction rates, diffusion processes and heat conduction are the determining processes.

THE ignition of combustible gas mixtures has attracted much theoretical and experimental attention. The areas mostly investigated are those concerned with ignition by extremely fast sparks and spontaneous self-ignition when the gases are contained in heated vessels. Mainly due to the work of B. LEWIS and G. VON ELBE[1], spark ignition led to the concept of 'minimum ignition energy' as an absolute value characteristic of the mixture under investigation. Spontaneous self-ignition temperatures are equally well investigated, and these values are of great technical importance (for values, see W. JOST[2]).

Between these two opposing areas, characterized by the concepts of minimum energy and minimum temperature, respectively, lies a large field of important ignition problems hardly investigated. For example, the ignition of combustible gases by electrically heated wires requires higher temperatures than the spontaneous self-ignition temperature of the mixture, and overall ignition energies are very large. In connection with the hazards of sparking electrical equipment, experiments are often conducted in which gases from an explosion within a vessel can escape through a channel between two flanges and frequently not ignite an explosive mixture outside, although a flame can momentarily be seen outside the flanges[3]. Connected with the latter problem is the question of safety of explosives used in coal mines, where hot gases released from the explosives must not ignite methane–air mixtures.

It was decided therefore to try to elucidate some of the problems involved by igniting combustible mixtures with hot gases or preferably with flames, since heat input and temperature could then be easily controlled. Hydrocarbon–air or hydrocarbon–oxygen mixtures were found to be difficult to investigate because of the very small ignition energies involved; stoichiometric methane–nitric oxide mixtures were therefore chosen for study after it was found that conveniently large flames could be burned within the surrounding methane–nitric oxide atmosphere without igniting the latter.

Experiments so far have been restricted to steady burning pilot flames as sources of ignition, and short-timed explosions have not yet been investigated.

EXPERIMENTAL ARRANGEMENT

The experimental arrangement was the simplest possible (*Figure 1*). A vertical outer tube of 6·0 cm inner diameter and 50 cm length was concentric with an inner tube on which a premixed laminar pilot flame burned. The

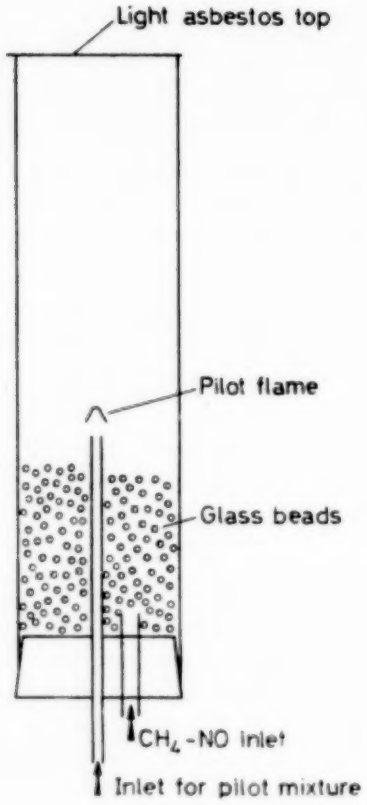


Figure 1. Experimental arrangement

inner tube was varied from 0·04 to 0·7 cm inner diameter, as the different fuel–oxygen–nitrogen combinations feeding the pilot flame demanded a variety of burner sizes. Unfortunately it is not possible to vary burner size and volume flow independently. After the pilot flame was burning, the outer tube was covered with an asbestos top to allow escape of the burned gases without back diffusion of air. Then a stream of stoichiometric methane–nitric oxide (50 or 100 cm^3/s) was admitted into the outer tube from below, and after this combustible gas mixture filled the tube ignition or non-ignition was observed. If the methane–nitric oxide mixture did not ignite, nitrogen could be withdrawn from the gases feeding the pilot flame until ignition occurred. Ignition usually resulted in a loud report.

For larger pilot flames the ignition process was more gradual and will be described in detail below.

RESULTS

Figure 2 shows results with a stoichiometric carbon monoxide–oxygen–nitrogen flame burning in an atmosphere of stoichiometric methane–nitric oxide. The ordinate represents the heat input of the pilot flame assuming complete combustion (that is, 1 cm^3/s carbon monoxide produces 3·02 cal/s)

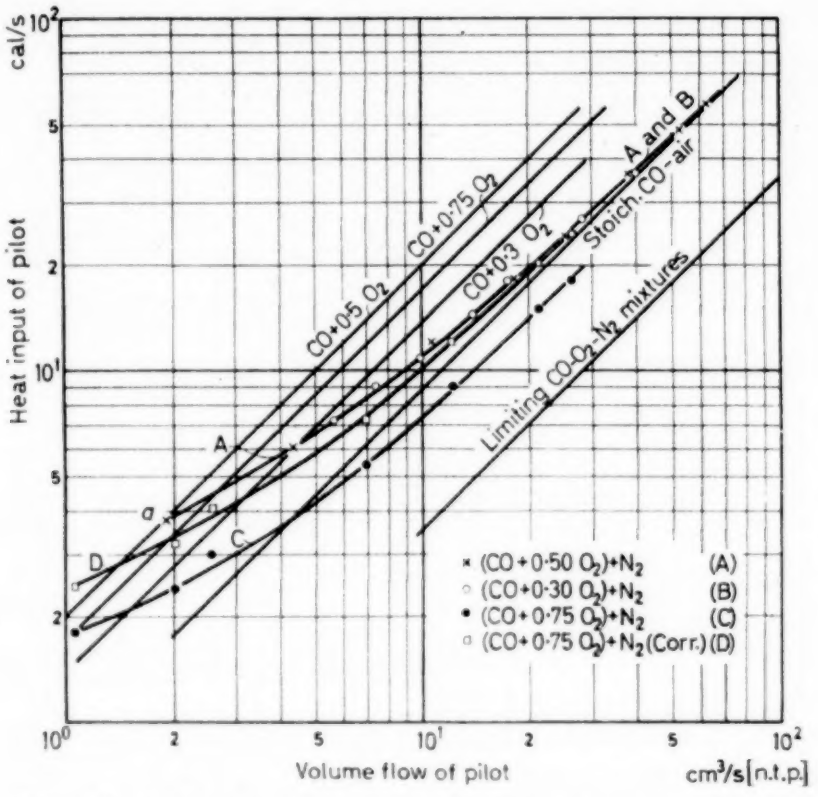


Figure 2. Ignition of stoichiometric CH_4 NO *mixtures by* CO–O_2–N_2 *pilot flames*

and the abscissa the volume flow of the pilot in cm^3/s (that is, the sum of carbon monoxide plus oxygen plus added nitrogen). In such a log/log plot all possible stoichiometric CO–0·5 O_2 flames lie on a straight line, and stoichiometric carbon monoxide–air flames are displaced toward higher volume flows. All stoichiometric carbon monoxide–oxygen–nitrogen pilot flames that can be experimentally realized lie between the CO–0·5 O_2 line and a line representing limiting carbon monoxide–oxygen–nitrogen mixtures which occur at a nitrogen/oxygen ratio of about 13·5. (For non-stoichiometric pilot flames see later.) Flames are also limited to a region above a certain minimum volume flow which, however, is below that represented on the graph. Curve A is the limit of stoichiometric carbon monoxide–oxygen–nitrogen pilot flames that will just ignite the surrounding methane–nitric oxide mixture. For example, point *a* represents the smallest CO + 0·5 O_2 flame without any nitrogen which ignites methane–nitric oxide. Smaller flames burn indefinitely in surrounding methane–nitric oxide without

igniting it. Curve A therefore indicates that the higher the volume flow of the igniting pilot, the more nitrogen can be added to the carbon monoxide–oxygen mixture until, for high-volume flows, curve A approaches asymptotically the carbon monoxide–air line; that is, stoichiometric carbon monoxide–air flames will just ignite methane–nitric oxide mixtures if they are large enough.

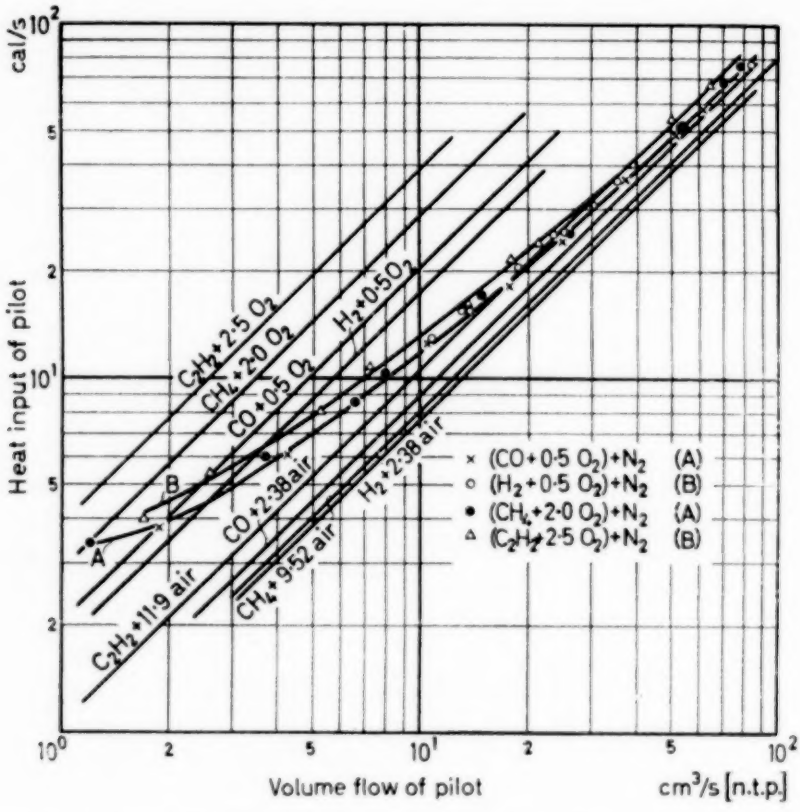


Figure 3. Ignition of stoichiometric CH_4–NO *mixture by* CO, CH_4, C_2H_2 *and* H_2 *pilots. (Pilots are stoichiometric with various amounts of* N_2 *added)*

Figure 3 shows similar curves for stoichiometric hydrogen, methane and acetylene pilots, with the carbon monoxide curve from *Figure 2*. All these curves run close to each other, and the total spread is not large. Carbon monoxide and methane are very close together (curve A), whereas acetylene and hydrogen are slightly higher (curve B). This has the effect that an acetylene–air pilot flame, for high-volume flows (within the experimental range), will barely ignite methane–nitric oxide as does the carbon monoxide–air flame, despite its higher temperature. Hydrogen and methane–air flames cannot ignite the surrounding methane–nitric oxide mixtures.

The limit (that is, just igniting) pilot flames can be characterized not only by their heat content, as is done in *Figures 2* and *3*, but also by their temperature. The result can be seen in *Figure 4*; the adiabatic flame

temperature was calculated using the tables in ref. 4. The temperatures of the methane and carbon monoxide pilots are again very close together, whereas acetylene and especially hydrogen are between 200° to 300° higher. The hydrogen pilot flame also does not seem to approach a constant

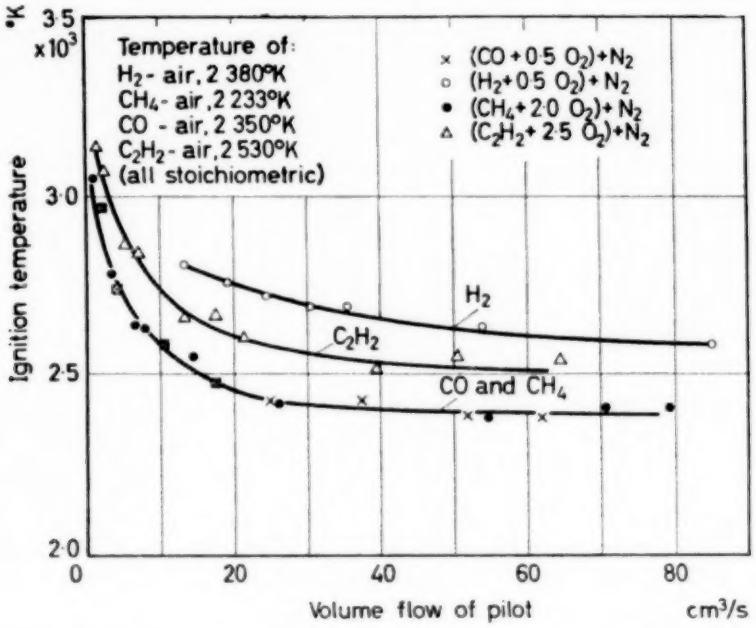


Figure 4. Ignition temperatures of H_2, C_2H_2, CO *and* CH_4 *pilot flames*

temperature for high-volume flows, as do the other pilot flames. For very low-volume flows the temperature requirements rise steeply but cannot of course be followed up beyond the corresponding temperature of the pure oxygen flame. With the acetylene and hydrogen pilot flames, even the pure oxygen flame was not investigated, as the flames were so small that the danger existed that too large a proportion of the heat liberated may have been absorbed by the burner. The hydrogen flame was, moreover, virtually invisible.

The influence of mixture strength of the pilot flame on ignition was measured for the carbon monoxide–oxygen–nitrogen system. The ignition curve for a $1\,CO + 0{\cdot}3\,O_2 + N_2$ (that is, rich carbon monoxide flame) is included as curve B on *Figure 2* and is within experimental error identical with curve A, which represents a stoichiometric pilot. For curve B the heat liberated, as plotted on the ordinate, is of course only that from carbon monoxide which can burn with the available oxygen. The fact that curves A and B are identical suggests that both pilots act as neutral sources of heat, without having specific catalytic effects. Lean pilots ignite much more easily, as can be seen from *Figure 2*, curve C, which represents $CO + 0{\cdot}75\,O_2 + N_2$ pilot mixtures. Here the full amount of the heat of combustion of carbon monoxide is taken in plotting curve C. It can be

argued that the excess oxygen will react with methane diffusing into the burned gases of the pilot flame and thus provide further heat. This can be taken into account by adding the heat of this reaction to that of the carbon monoxide–oxygen reaction, and curve D is thus derived. For high-volume flows of the pilot, curve D seems to approach curves A and B; however, for low flows large deviations persist. Oxygen seems therefore to have a specific influence on the methane–nitric oxide ignition, a property that seems to vanish as oxygen is increasingly diluted with nitrogen for the larger flows.

To test the relative importance of flame temperature and of total heat input, argon and carbon dioxide were substituted for nitrogen in carbon monoxide–oxygen–inert gas pilots. Although the critical heat input (in cal/s) was changed by use of carbon dioxide and argon instead of nitrogen, the limiting flame temperatures coincided with those with nitrogen in equivalent pilot flame mass flows.

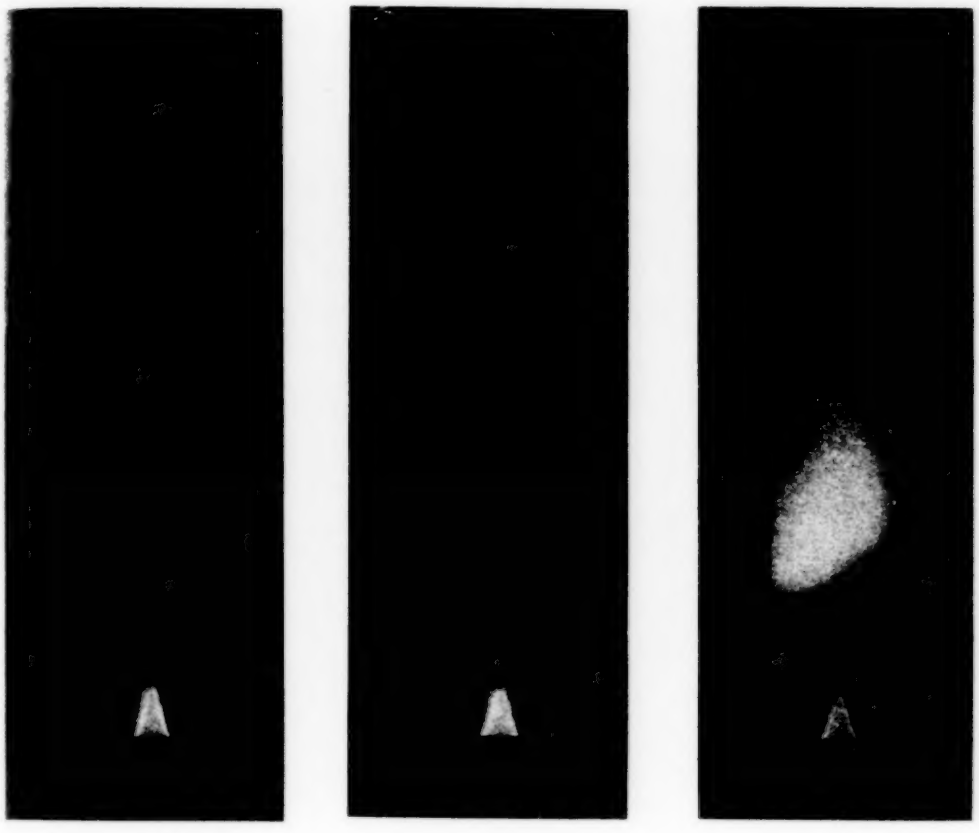
The ignition of stoichiometric methane–nitric oxide mixtures by small hot pilot flames is too rapid a process to follow in detail. Interesting information, however, may be gained by observing the same ignition process with large and cooler pilot flames. *Figure* 5(a) is a picture of a carbon monoxide–oxygen–nitrogen pilot burning in a stoichiometric methane–nitric oxide mixture. When the amount of nitrogen in the pilot is reduced from 19·5 to 19·0 cm^3/s, a column of luminosity appears in the centre of the hot pilot gases, which were so far invisible, indicating reaction of methane and nitric oxide, which diffuse into the centre of the hot column [*Figure* 5(b)]. On further reducing nitrogen by a very small amount, a bright bluish flame appears to grow from this centre of the column far above the actual pilot flame and spreads in all directions throughout the outer vessel [*Figure* 5(c)].

It was also attempted to use diffusion flames as igniting pilots. The results were less reproducible, especially if the burner tube consisted of two concentric tubes with the annulus carrying the oxygen. Some oxygen seems to escape its primary combustion and therefore to catalyse the methane–nitric oxide ignition. This seems also to be the reason why ignition depended on burner size and shape, as this influenced the escape of some oxygen. It is also possible to use no fuel at all for the pilot, but to burn an oxygen–nitrogen mixture directly, with the outside methane as a diffusion flame. On introduction of nitric oxide into this methane, ignition and non-ignition can be observed. The subject, however, is outside the scope of this paper, especially as the pilot in this arrangement is no longer an independent flame or hot-gas supply.

DISCUSSION

In ignition experiments using instantaneous sparks as heat sources, it was found[1] that a minimum energy is required to obtain ignition. Equally, if a continuously electrically heated wire is suspended in a combustible mixture we can measure the total energy input (in cal/s), as well as the temperature of the wire necessary for ignition. If the wire were made large enough

(that is, virtually a furnace containing the gas) the energy requirements become meaningless, but the temperature required will be the spontaneous ignition temperature of the mixture in question. If the wire were exceedingly small and the temperature very high, it would conceivably be possible



(a) (b) (c)

Figure 5. (a) *Pilot* (CO *12·0 cm³/s;* O_2 *6·0 cm³/s;* N_2 *19·5 cm³/s) burning within stoichiometric* CH_4–NO *mixture;* (b) *as* (a) *but* N_2 *reduced to 19·0 cm³/s;* (c) N_2 *reduced to 18·5 cm³/s.* CH_4 NO *flame starts expanding from hot column visible in* (b)

to express the ignition requirement only as an energy requirement (in cal/s). Intermediate cases will be characterized by a statement of both temperature and energy. The pilot-flame experiments discussed above give values of temperature and energy requirements over a wide range of flame sizes for ignition of stoichiometric methane–nitric oxide mixtures, and it is possible to extrapolate toward zero pilot-flame flow. *Figure 6* shows the same curves as *Figure 3* but on a linear scale. Fuel–oxygen and fuel–air flames are again represented by straight lines starting at the origin. The curves representing igniting pilot flames are also straight lines within experimental error, but they cut the ordinate at about 2·5 cal/s. This value is the minimum energy (cal/s) necessary for igniting methane–nitric oxide mixtures, if the energy were delivered at a point source of very high

temperature. This conclusion is strengthened by the fact that this value is independent of the nature of the pilot gases, as all curves can be extrapolated toward this value. Ignition by hot neutral gases therefore can be represented by the following simple equation

$$\text{Ignition energy [cal/s]} = B \times \text{volume of pilot [cm}^3\text{/s]} + C\,\text{[cal/s]}$$

B has the dimension of cal/cm^3, from which the temperature of the pilot

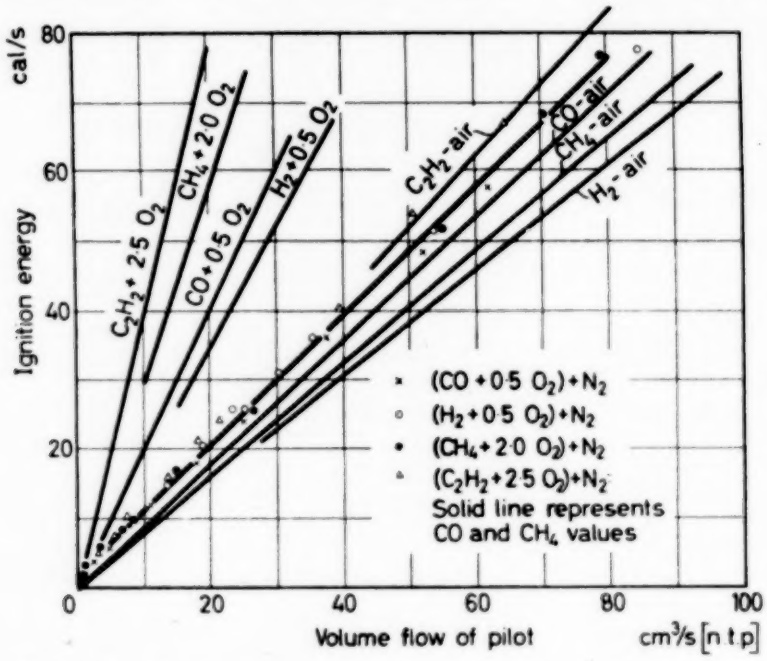


Figure 6. Ignition energies of H_2, CO, CH_4 *and* C_2H_2 *pilot flames*

can be derived, when the volume flow of the pilot is very high; that is, C can be neglected compared with $B \times$ volume flow. As regards acetylene and carbon monoxide pilots, this temperature is virtually the temperature of the respective air flame. As the volume flow decreases, C cannot be neglected, and for disappearing volume flow C is the minimum energy flow for ignition of methane–nitric oxide mixtures for continuously running energy delivery. Fortunately the temperatures of stoichiometric oxygen flames are high enough to make this extrapolation very certain; that is, the ignition energies of oxygen pilots are already very close to the extrapolated values with zero mass. Large and cooler acetylene and especially hydrogen pilot flames need slightly higher energy input than methane and carbon monoxide flames for methane–nitric oxide ignition. This cannot be explained by the different values of the specific heat of the product gases, as the temperature plot of *Figure 4* accentuates these differences. It is possible that the much higher burning velocities of the acetylene and hydrogen pilot flames lead to a higher jet velocity of the hot pilot gases, even high above the reaction zone, where ignition of the outside atmosphere occurs. Data so far available do not make it possible to account for the ignition process in terms of contact time and activation energy. It seems

reasonable, however, to assume that high pilot gas velocity is detrimental to the ignition process.

The minimum energy flow for continuously delivered energy (cal/s) will certainly be related to the minimum ignition energy for instantaneous ignition (cal). This latter value is about 10 millijoules*. Minimum energy flow for continuous ignition of the same mixture strength is 2·5 cal/s ($\sim$10 J/s). The time factor is therefore about 10^{-3} sec. The theoretical significance of this factor is outside the scope of this paper and will therefore not be discussed here.

The temperature of a large laminar pilot flame required for ignition becomes independent of pilot size and may be a significant value. This temperature is not identical with the spontaneous ignition temperature, from which it differs in two important respects. The surfaces of the heated vessels necessary for determining the spontaneous ignition temperature are absent, and heterogeneous reactions are ruled out. More important is the fact that heat is delivered from the pilot gases to the combustible mixture with mass addition. It has been noted that the combustible mixture begins to react inside the core of the hot pilot gases, where methane and nitric oxide are delivered by diffusion. Diffusion and heat conductivity are interrelated phenomena and no combustible mixture can diffuse to this region without heat being lost to the outside. The boundary of the hot pilot gases can theoretically never reach temperatures higher than half the adiabatic flame temperature of the pilot. Ignition is therefore favoured in regions of small methane and nitric oxide concentrations at high temperature compared with high concentrations at low temperature.

The spontaneous self-ignition temperature of stoichiometric methane–nitric oxide mixtures was separately determined in a ceramic tube (Norton RA98) within a platinum furnace[5]. The value may depend on surface conditions but was very reproducible in our arrangements at 1 110°C. This shows that ignition by a large volume of hot gases leads to an ignition temperature significantly higher than the spontaneous ignition temperature, so that it may be appropriate to give this temperature a name; it is suggested that it be called 'hot-gas ignition temperature', because it is the hot burned gases which lead to ignition and not the flame as such. This temperature is very important in many practical applications. It is hoped to report on hydrocarbon ignition in the near future.

This work was sponsored by Project SQUID which is supported by the Office of Naval Research under contract Nonr 1858(25), NR-098-038. Reproduction in full or in part is permitted for any use of the U.S. Government. Figures 1 to 6 are reproduced by courtesy of the U.S. Bureau of Mines.

Division of Explosives Technology,
Bureau of Mines, Region V,
U.S. Department of the Interior,
Pittsburgh, Pennsylvania

(Received September 1957)

*We are indebted to M. V. Blanc for a determination of this value.

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Application of Well-stirred Reactor Theory to the Prediction of Combustor Performance

H. C. HOTTEL, G. C. WILLIAMS and A. H. BONNELL

It is shown that some gross performance characteristics of combustion chambers can be simulated by conceptual models composed of interacting elements the performance of each of which can be inferred from a knowledge of well-stirred reactor behaviour. Analyses are made of three different models to show the effect of element interaction due to: (1) pressure differences between elements, (2) recirculation between elements, and (3) non-uniform fuel/oxidant ratio distribution. The predicted performance of these models exhibits discontinuities and instability phenomena paralleling those found experimentally. Experimental work to date indicates the utility in analysing high-output combustion chamber performance of models based on simple combinations of well-stirred reactors.

MIXING has long been recognized as the dominant phenomenon in many industrial combustion processes. However, there has been a growing realization that chemical reaction rates often place important limitations on the performance of high-output combustors. This has led in recent years to the study of the well-stirred reactor from both a conceptual and an experimental standpoint.

The intensity of combustion in practical high-output combustors lies between that of mixing-controlled industrial furnaces and reaction-rate-limited well-stirred reactors. In principle, then, the analysis of this class of combustors must allow for interaction between mixing and chemical rate phenomena. Both of these are highly complex, and their interactions lead to such unusual results as wide or sometimes discontinuous variations in combustion efficiencies and/or flow patterns in response to variations in firing rates. One might hope to simplify the problem by treating the performance only in terms of mixing rates or in terms of chemical kinetics; but one would expect in this approach to have to change conceptual models with a change in the range of firing rates.

Another approach might consist of identifying the modest efficiency of a practical combustor with that of a well-stirred reactor of the same firing rate but of much smaller volume, and in making the assumption that the departure of practical chambers from well-stirred reactor performance is due solely to incomplete use of the volume available. One would not expect so simple a model to fit over any extreme range of operating variables. If, however, one were to postulate a combustor composed, not of just one well-stirred reactor volume and void volume, but of a small number of volumes, characterized variously as stirred reactors, plug-flow reactors,

recirculating volumes, cold-mixing volumes and void volumes, which are connected in parallel, series, or series–parallel flow combinations, one could fit such a conceptual model to a wide range of variations in the operating variables. The result would not be impressive, however, unless it were found that the complex performance of practical combustors can be predicted by a relatively simple conceptual model of the compound character described above. It is the object of this paper to indicate the performance predictions possible from several such models.

PREVIOUS WORK

Well-stirred reactor theory has been used by W. H. AVERY and R. W. HART[1] in an analysis of a can-type combustor based on assumptions of: (*a*) instantaneous mixing transverse to the flow direction, (*b*) no mixing in the flow direction, and (*c*) addition of fuel/air mixture along the length of the combustor. To find the performance of the combustor, integration of reaction progress was performed in the flow direction on the basis of an assumed conventional *n*th order rate equation. Burnedness and temperature were assumed uniquely related, the variation of kinetic energy along the flow path being ignored. P. ROSEN and R. W. HART[2] amplified this model, and included allowance for kinetic-energy effects. E. A. DEZUBAY[3] has proposed another model of a combustor in which allowance is made for the addition of secondary air. In DeZubay's model, combustion was postulated to occur in two well-stirred zones, rather than in a long, plug-flow chamber. The first of these zones was fed with a relatively rich fuel/air mixture, the second with the products of combustion of the first reactor together with secondary air. Neither of these two models allows for the effect of recirculation on combustor performance—an effect generally considered to be significant, especially in stability phenomena. A third group of combustion models was offered by W. G. BERL, J. L. RICE and P. ROSEN[4] depicting the combustion process in terms of various patterns of flame kernels, each undergoing laminar burning.

After the major portion of the work on this paper was completed, D. B. SPALDING[5] published a paper in which he analysed pressure-drop requirements in a combustion chamber in terms of a model involving recirculation of burned gases. This paper is of special interest since Spalding's model chamber is almost identical to the recirculation model presented in this paper. Spalding considered a combustor in which the flow pattern was circulatory, with the circulation path divided into two portions. In the first portion, fresh feed was mixed with recirculated gases, and a part of the mixture was recirculated, the balance leaving the combustor as burned gases. In this mixing section no allowance was made for combustion. In the second portion, the recirculation zone, combustion occurred in a plug-flow pattern. Like the previous analyses, this one was aimed at relating the performance of a real combustor to experimental or theoretical stirred-reactor behaviour; its allowance for the effect of recirculation in the chamber constituted a significant improvement over the earlier analyses.

WELL-STIRRED REACTOR THEORY

In the models to be discussed the well-stirred reactor is used to relate the combustion rate to the composition. Hence it is in order to review briefly the concepts on which the well-stirred reactor, first suggested by J. P. LONGWELL and M. A. WEISS[6] and later elaborated by others[7–9], is based.

Let the overall reaction be

$$\mathrm{F} + a\mathrm{O}_2 \rightarrow p\mathrm{P}$$

and let ϕ times the stoichiometric fuel be used. If the identifiable components of the mixture at any stage of completion of combustion are complete-combustion products plus unconsumed fuel and/or oxygen, specification of a single quantity, for example, β, the burned fraction of the fuel fed, is sufficient, together with stoichiometry, to identify the mixture. For each additional component assumed to be present, one more quantity, γ, δ, etc., must be specified to fix the composition; and the choice of how best to define the new term will depend on the postulated chemistry of the process. The mole fraction, f_X, of any component X is thus representable as $f_X(\phi, \beta, \gamma, \delta, \ldots)$, or for a fixed value of ϕ, as $\bar{f}_X(\beta, \gamma, \delta, \ldots)$; and the single argument β is sufficient for the simplest possible picture of the combustion process.

The well-stirred reactor is by definition a chamber in which the composition, measured at the inlet by β_0, γ_0, δ_0, changes instantly to values measured by β, γ, δ; and the composition is everywhere that of the outlet. In this system, the temperature T is fixed by the composition, and for a fixed ϕ can be represented as $\bar{f}_T(\beta, \gamma, \delta, \ldots)$. For the simplest case in which the product composition, and consequently T, is fixed by β, it is obvious that either β or T may be used as a measure of combustion progress or burnedness. Assumption of linearity between the two, leading to the relation $\beta = (T - T_0)/(T_{af} - T_0)$, simplifies the numerical work, but is not necessary.

As many chemical rate equations are required as there are arguments β, γ, δ, ... required to fix the composition. The present treatment will be restricted to the simplest description of the combustion, requiring only one rate process to be formulated. This is most conveniently the rate of consumption of fuel, given by

$$-\mathrm{d}N_\mathrm{F}/\mathrm{d}t = VT^{0.5}k' \exp(-E/RT) \times C_\mathrm{F}^{a} C_{\mathrm{O}_2}^{n-a} \qquad \ldots . [1]$$

on the assumption that the reaction is of overall nth order and of order a in fuel. Substituting $\bar{f}_\mathrm{F}(\beta) \times P/RT$ for C_F and $\bar{f}_{\mathrm{O}_2}(\beta) \times P/RT$ for C_{O_2}, one has

$$-\frac{\mathrm{d}N_\mathrm{F}}{\mathrm{d}t} = VP^n \frac{k' \exp(-E/RT)}{R^n T^{n-0.5}} \times \bar{f}_\mathrm{F}(\beta) \times \bar{f}_{\mathrm{O}_2}(\beta) \qquad \ldots . [2]$$

Since T and β are uniquely related, equation 2 may be written

$$-(\mathrm{d}N_\mathrm{F}/\mathrm{d}t)/VP^n = \psi_1(\beta) \qquad \ldots . [2a]$$

In a well-stirred reactor fed at the molal fuel feed rate G, with burnedness changing from an inlet value β_0 to an outlet value β, the fuel consumption

rate is $G(\beta - \beta_0)$; this replaces $-dN_F/dt$. Then one has

$$G/VP^n = \psi_1(\beta)/(\beta - \beta_0) \quad \ldots . [3]$$

and for a reactor being fed an unburned fuel/air mixture ($\beta_0 = 0$), this may be written

$$G/VP^n = \psi_1(\beta)/\beta = \psi_2(\beta) \quad \ldots . [4]$$

A typical curve representing this relation appears as *Figure 1*.

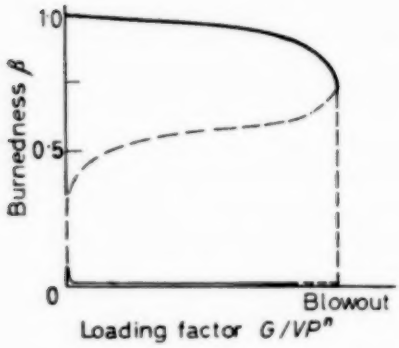

Figure 1. Simple well-stirred reactor

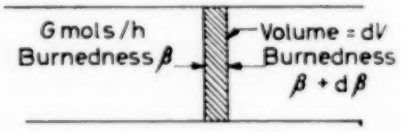

Figure 2. Plug-flow reactor

Since the significance of curves like *Figure 1* has previously been discussed in detail[8, 9], it will only be noted here that of the three values of β for a given value of G/VP^n in certain ranges, the top represents stable burning, the bottom a cold, non-burning system, and the middle branch an unstable solution, or, if one wishes, the condition for ignition.

Because the performance characteristic of two-stage stirred reactors, multi-stage stirred reactors, and plug-flow reactors can all be derived from the basic rate equation 2 or 2a, they are of course inter-related. Consider first the plug-flow reactor (*Figure 2*). Such a reactor may be pictured as an infinite series of infinitesimal well-stirred reactors in tandem. Since the flow rate through each of these is the same, they are best considered as stirred reactors in which volume is the variable, and hence equation 3 is inverted to give

$$VP^n/G = (\beta - \beta_0)/\psi_1(\beta) \quad \ldots . [5]$$

For a typical slab of a plug-flow reactor, having a volume dV, being fed with reactants of composition β, and discharging products of composition $\beta + d\beta$, equation 5 yields the relation

$$(P^n/G)\,dV = d\beta/\psi_1(\beta) \quad \ldots . [6]$$

If the reaction-rate function ψ_1 is available, as for example from a postulated chemical mechanism of combustion, equation 6 can be integrated directly to give the performance of a plug-flow reactor. If, however, the function ψ_2 is available, for example from a stirred-reactor experiment, it can be used directly to solve equation 6. The latter may be written

$$(P^n/G)\,dV = [\beta/\psi_1(\beta)]\,[d\beta/\beta] = [1/\psi_2(\beta)]\,d\ln\beta \quad \ldots . [7]$$

or, integrating between the limits $\beta=\beta_0$, $V=V_0$ and $\beta=\beta$, $V=V$

$$(P^n/G)(V-V_0)=\int_{\ln\beta_0}^{\ln\beta}(\mathrm{d}\ln\beta/\psi_2\beta) \qquad \ldots.[8]$$

If, then, one plots the stirred-reactor performance curve in the form $1/\psi_2(\beta)$ against β on a logarithmic scale, the area under the curve from β_0 to β (see *Figure 3* with x and y coordinates reversed to correspond to previous plots) represents the generalized volume $(V-V_0)(P^n/G)$ necessary to carry out that much reaction in plug flow; and that area can be plotted on the same curve (dotted line). In *Figure 4* the result of integration of

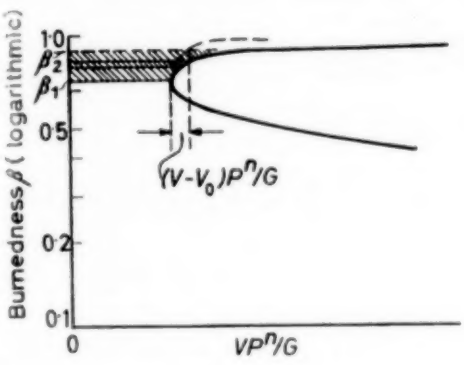

Figure 3. Integration of well-stirred reactor curve to find plug-flow reactor curve

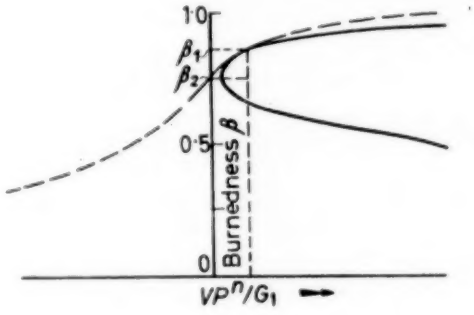

Figure 4. Plug-flow reactor curve

equation 8 over the full range of β is shown on arithmetic coordinates (the broken curve represents plug-flow performance) together with the basic stirred-reactor curve. The plug-flow curve has been displaced laterally to be tangent to the other at a generalized volume $[VP^n/G]_1$, the significance of which requires comment. In a plot of β versus $1/\psi_2(\beta)$ on arithmetic coordinates, the point of tangency of a line from the origin represents a stirred reactor operating at the maximum possible burning rate per unit volume, and the condition for this point is

$$\beta/(1/\psi_2)=\mathrm{d}\beta/\mathrm{d}(1/\psi_2) \qquad \ldots.[9]$$

Noting from equation 4 that the LHS of equation 7 for a plug-flow element may be represented as $\mathrm{d}(1/\psi_2)$, one sees that equation 7 is of the same form

$$\mathrm{d}(1/\psi_2)=\mathrm{d}\ln\beta_2/\psi_2 \qquad \ldots.[10]$$

as equation 9; i.e. at that β, V combination corresponding to the maximum burning rate in a stirred reactor, the value of $\mathrm{d}\beta/\mathrm{d}V$ is the same for the stirred and plug-flow reactors. This corresponds to the point $[VP^n/G]_1$ of *Figure 4*. Note that for any value of β above β_1, the incremental volume required in a plug-flow reactor is less than that in a well-stirred reactor, but to increase the burnedness from any point lying between β_2, the stability limit of the stirred reactor, and β_1 to the value β_1, a greater volume

is required in a plug-flow than in a well-stirred reactor. For points below β_2, the well-stirred reactor is unstable. The minimum total volume required to accomplish any burnedness β (lying above β_1) is then accomplished in a well-stirred reactor operating to give products at β_1, followed by a plug-flow reactor.

It is noticed that the plug-flow curve of *Figure 4* looks very much like the profile of a laminar flame front in which burnedness has been plotted against L/S_L, the measure of time. However, in the calculation for *Figure 3* there is no allowance for diffusion of heat or mass such as gives rise to a laminar flame propagation rate, and although the abscissa has dimensions proportional to a length/flame speed ratio, there is no definite distance associated with the abscissa; consequently, there is no analogue to a wave propagation.

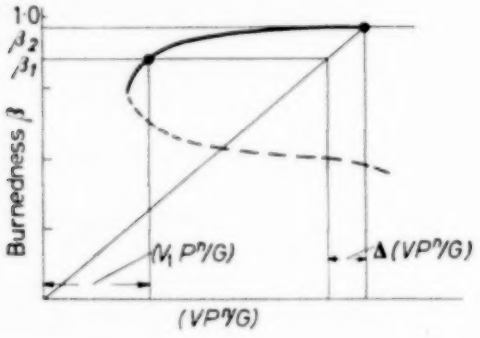

Figure 5. Well-stirred reactor being fed a partially burned feed

The performance of a well-stirred reactor being fed a partially burned feed is readily obtained from the primary stirred reactor curve as indicated in *Figure 5*, in which β is plotted against $1/\psi_2(\beta)\,(=VP^n/G)$. The slope of a line from the origin to a point on the curve represents the burning rate per unit volume in any system in which the burnedness is β. Since when the feed is partially burned the burnedness to be accomplished is $\beta-\beta_0$ rather than β, the generalized volume necessary is $(VP^n/G)(\beta-\beta_0)/\beta$. This appears in *Figure 5* as the Δ of VP^n/G. *Figure 5* can also be considered an example of operating two reactors in series. The first reactor fed with the unburned fuel ($\beta_0=0$) requires the volume V_1P^n/G to deliver products of composition β_1 and the second reactor fed with products of burnedness β_1 and delivering products of burnedness β_2 requires the additional volume $\Delta VP^n/G$. As long as operation of the first reactor is represented by a point on *Figure 5* to the right of the point of tangency of the curve to a straight line through the origin, the volumetric heat release rate for the pair is always greater than that of a single well-stirred reactor giving the same final burnedness.

COMBUSTION CHAMBER MODELS

In the combustion chamber models presented here, the problem is simplified by dividing a chamber into zones which behave as simple chemical reactors either well-stirred or plug-flow. The zones are connected by flow lines indicating the fluid flow patterns of the chamber.

In any real combustor several types of zones may be expected. With a jet of fuel–air mixture feeding a chamber one expects a relatively unburned zone to exist in the central core. Around the sides of the jet the more nearly burned gases in the recirculation zones are in a nearly well-mixed region because of the intense turbulence created by the central jet. In the corners of the chamber, regions of inactivity are expected since these regions are relatively stagnant. If the fuel and air are fed separately into a moderately well-stirred chamber, similar zones are expected. However, in this case one finds in addition variations in the fuel/air ratio in various portions of the chamber.

In the models values must be assigned to the recirculation rate, the relative sizes of the central core and recirculation zones and the variations in fuel/air ratio. These values are associated with chamber design variables. To the extent that reasonable values may be associated with the theoretical models the models may be held successful.

Two-stability-limit model

Three conceptual models have been developed which predict some of the phenomena of practical combustors. One of these phenomena is the abrupt change in flow pattern observed in some combustors as the feed rate is increased; when a certain rate is reached the flame in one portion of the chamber disappears, with accompanying adjustment of the flow pattern. This behaviour has been observed in a two-dimensional chamber fed by a single jet of a fuel–air mixture. A simplified conceptual model of such a jet–chamber combination will now be presented.

Figure 6 shows such a chamber with the fuel–air mixture entering at the bottom and products leaving at the top. Let the dotted lines bound the edges of those areas, taken normal to the axis of flow, through which the total upward gas flow is constant and equal to the feed rate. The dotted lines thus represent surfaces through any element of which there is no net mass flow; but there is equal and opposite turbulent transport through them. Because the zones external to the central core are fed with charge which, on the average, is less burned than the gas which returns to the central core, the mean gas temperature in the outer zones is higher than that of the central core. Consequently, the linear velocity of the outwardly moving gas is less than that of the inwardly moving, more completely burned gas; and the force producing this net inward momentum flux is a higher static pressure existing in the outer zones.

If both recirculation zones are active, then the pressure effects on the two sides counterbalance: but if one zone is active and the other inactive a pressure imbalance occurs, causing a deflection of the jet toward the inactive side. This increases the volume of the active zone, thereby improving the opportunity for completion of combustion in it. The end effect is a bending of the jet, in response to the pressure exerted by the larger recirculation zone, to a position of equilibrium between the jet-momentum force and the pressure-area force of the hotter recirculation zone.

Since the system is two-dimensional, the difference in the volumes of the recirculation zones may be assumed proportional to the pressure difference between them. And since the pressure effect is postulated to be a result of a transverse momentum flux, the pressure difference between the two recirculation zones should be roughly proportional to their temperature difference. To simplify this treatment the central zone will be assumed a high-speed non-reacting jet stream in which the gases reside for a relatively short time, serving solely to supply feed gases to the recirculation zones; and the latter zones will be considered well-stirred reactors.

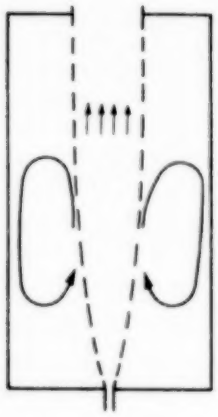

Figure 6. Physical picture

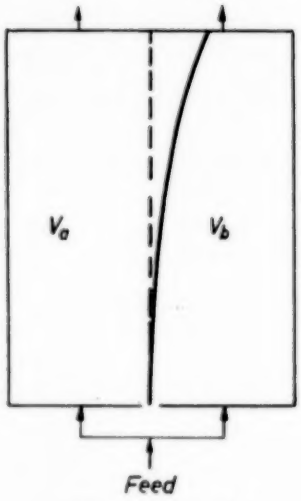

Figure 7. Model

The block diagram representing this model, *Figure 7*, is two well-stirred reactors of constant total volume separated from each other by an elastic barrier zone and the jet, which has the property of so bending in response to pressure differences that the change in volume of either of the reactors is directly proportional to the pressure difference between the two. In the absence of a pressure difference the system is symmetrical. The fuel–air mixture will be assumed to be fed equally to the two reactors.

The deflection of the barrier is expressed in terms of the difference between the volumes of the two reactors

$$\tfrac{1}{2}(V_a - V_b) = k_1 (P_a - P_b) \qquad \ldots . [11]$$

and the pressure difference created by a difference in burnedness in the two reactors is

$$(P_a - P_b) = k_2 (\beta_a - \beta_b) \qquad \ldots . [12]$$

Assume a well-stirred reactor performance curve available (*Figure 8*) giving the relation between burnedness and normalized volume.

The problem is to examine the effect, on the models described, of arbitrarily creating a volume difference $V_a - V_b$ between the two reactors to see if the resulting difference in burnedness, $\beta_a - \beta_b$, will produce a $P_a - P_b$ sufficient to maintain the barrier in its deflected position. Let the

total volume/feed ratio, equal to the initial ratio for each reactor, be represented by point O of *Figure 8*. Let the barrier be deflected by an amount $\frac{1}{2}(V_a - V_b)$, causing zones a and b to increase and decrease respectively by this amount. These volume changes are accompanied by corresponding changes in burnedness which may be found from *Figure 8*, where the points a and b represent the new volume/feed ratios of sides a and b. Solutions for the new volume/feed ratios exist on the branches

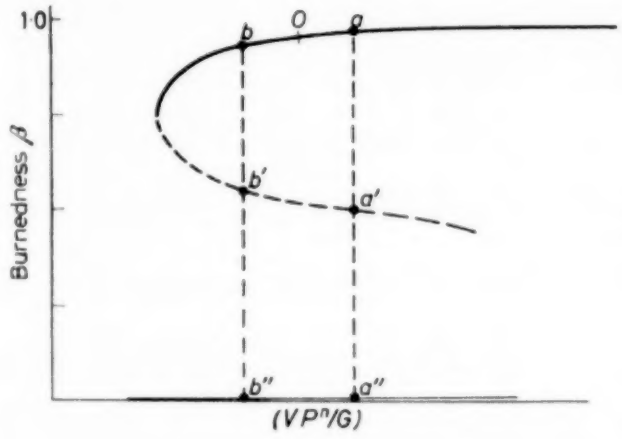

Figure 8. Well-stirred reactor curve for two-stability-limit model

at a and a'' and b and b'' (a' and b' are thermally unstable reactor conditions). These burnedness differences, four of them (plus five involving unstable reactor conditions) can be evaluated, and from equation 12 the corresponding $(P_a - P_b)$s can be found. These are plotted as branches I and II* of *Figure 9*. Those portions of the curves which involve thermally unstable reactor conditions, i.e. the dotted part of *Figure 8*, are dotted.

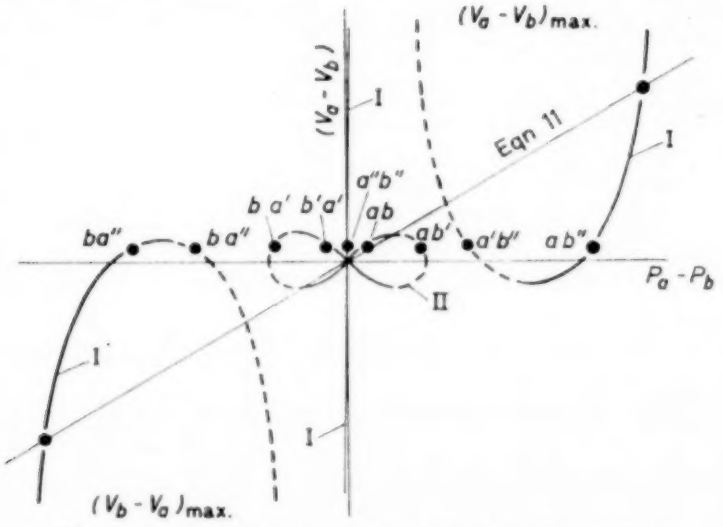

Figure 9. Performance of two-reactor model at fixed volume/feed ratio and feed composition

*Loop II as drawn may be misleading. The only symmetry intended is that about the origin, not about either axis.

The *ab* solution occurs when both reactors are hot, and a low $P_a - P_b$ is developed, lying on branch II in the first quadrant. If side *b* is blown out, a high $P_a - P_b$ is developed at the point *ab''* on branch I, also in the first quadrant. Similar reasoning leads to the remainder of the points. Use of other values (both negative and positive) of $V_a - V_b$ for the same value of point *O* of *Figure 8* permits completion of the branches I and II of *Figure 9*. For each new value of total volume/feed ratio (i.e. a new value of point *O*, *Figure 8*) a new pair of branches I and II will be generated. It will be noted that at a sufficiently high feed rate the reactor pair will just be able to operate with both sides active. This occurs when point *O* is at the blowout point of the well-stirred reactor curve of *Figure 8*. If the feed rate to the same reactor pair is increased further, it may still be possible for one side of the model to operate on the stable 'hot' branch of the reactor curve if the barrier is deflected sufficiently; however, since the maximum volume difference possible occurs when V_a is twice its initial value, the maximum feed rate which permits a possible 'hot' solution is twice the feed rate corresponding to the above blowout point.

To find the stable operating points on *Figure 9*, the line representing equation 11 is superimposed on curves I and II for the specific *O* chosen (a non-linear relation between $V_a - V_b$ and $P_a - P_b$ could be used as well). The equilibrium values of $V_a - V_b$ are found at the intersections of the line of equation 11 with either branch I or branch II. Branches I and II and the curve of equation 11 are symmetrical about the origin, signifying that it makes no difference which side becomes colder. Three stable solutions are found, the origin and the outermost intersections. Of the remaining four intersections, two are unstable (*a'b''* and its symmetrical counterpart) because one side of the reactor is operating on the unstable branch of the well-stirred reactor relation, and two are unstable (the symmetrical *ab* solutions) because the barrier is in a metastable position. A stable barrier position is one in which a momentary change in $V_a - V_b$ causes a change in $P_a - P_b$ such that a net restoring force results. This means that at a stable intersection of the branches I or II with the line of equation 11, both curves must have a positive slope and the slope of the former must be greater than that of the latter.

Consider the effect of increasing the feed rate in a system of the same total volume as before. Point *O* of *Figure 8* will move toward the β axis. As it approaches the nose of the curve of *Figure 8*, branch II of *Figure 9* becomes smaller and thinner (i.e. its slope at the origin becomes smaller and its x intercept approaches the origin). This change in operating conditions probably has a negligible effect on the slope of the curve representing equation 11 because the increased pressure difference resulting from the increased feed rate will keep pace approximately with the increase in jet momentum force. When branch II becomes a tangent to the curve of equation 11 at the origin (*Figure 10*) the origin becomes an unstable intersection. Hence the only remaining stable solution corresponds to having one side blown out and the other burning stably. This will call for a sudden shift in $V_a - V_b$, a fact which is experimentally observed.

Continually increasing the feed rate will cause the disappearance of branch II, and eventually branch I will become a tangent to the line of equation 11 (*Figure 11*). This represents the condition for the total blowout of the chamber.

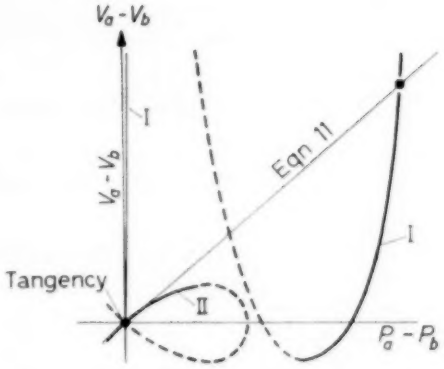

Figure 10. One-sided blowout condition for two-reactor model

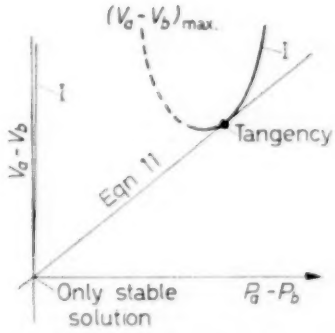

Figure 11. Total blowout condition for two-reactor model

This model also has interesting implications concerning behaviour at other chamber feed rates. *Figures 12*(a) to (f) represent six feed rates with six corresponding pairs of branches I and II along with a common curve showing the jet stiffness independent of flow rate. (This time only the stable portions in the first quadrant of *Figure 9* are shown.) On each of these diagrams a horizontal dotted line is drawn as a tangent to the nose of branch II. This represents the blowout point of branch II, i.e. the maximum volume difference allowable for a given volume/feed ratio if both zones are to be simultaneously stable. If $V_a - V_b$ is below this limit either the smaller side will burn stably or, if it is blown out, it may be relighted by a sufficiently strong source; and if $V_a - V_b$ exceeds this level, the smaller side will be blown out.

Consider a chamber operating at a volume/feed ratio represented by *Figure 12*(b) and with both sides active, i.e. with operation at the origin of *Figure 12*(b). If a disturbance, $V_a - V_b$, is imposed on the jet, the latter will tend to return to its central position unless the $V_a - V_b$ imposed is greater than the blowout limit represented by the dotted line. If this limit is exceeded, then one side will become cold and a high $P_a - P_b$ will be developed, and the jet will move to the one-sided blowout position instead of returning to the central position. If the chamber is operating at the one-sided blowout position when the $V_a - V_b$ is imposed, then the reverse argument is applied; however, in this case the problem of re-light must be considered. Even if the disturbance is large enough to bring the small side to a re-lightable position, the small side will not re-light if the ignition source is too weak, and the jet will return to the one-sided blowout position. Since in this case the disturbance required to reach the critical level is much larger than in the first case, it would be predicted that the one-sided blowout position would be the more stable one.

At a lower feed rate than that of *Figure 12*(b), such as that represented by *Figure 12*(c), the blowout point of branch II is centrally located with respect to the two stable jet positions. In a highly turbulent combustor which has in addition high radiant heat transfer rates from hot walls to cold walls, it is easy to imagine that, if the volume/feed ratio for any cold zone is above the minimum required for stability by the well-stirred reactor kinetics, ignition will occur. If simultaneously there is an equal likelihood that a disturbance in $V_a - V_b$ from either stable jet position will cross the critical blowout level, conditions for a flickering flame exist.

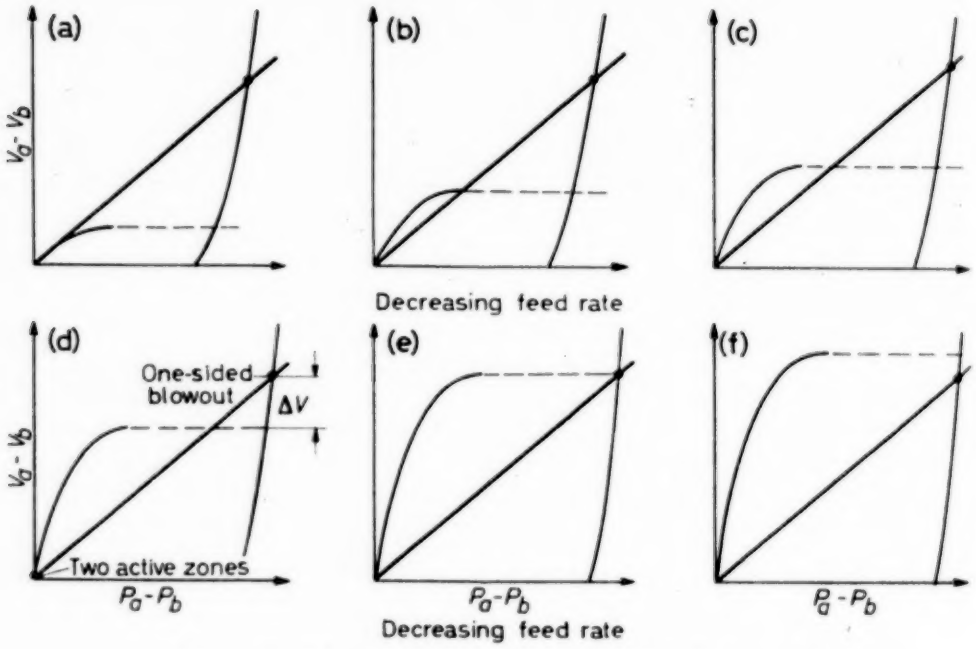

Figure 12. Effect of feed rate on two-stability-limit model

At even lower feed rates, represented in *Figure 12*(d), the situation is reversed from that represented by *Figure 12*(b). In *Figure 12*(d) the two-active-zone solution is relatively more stable since a smaller disturbance is required to go from the one-sided-blowout position to the maximum re-light level than in the opposite direction.

In *Figure 12*(f), the feed rate is so low that the one-sided-blowout solution is below the critical blowout level of branch II. Thus, assuming that re-light will always occur if the opportunity exists, the only stable solution at this rate is the origin (two active zones).

This type of reasoning leads to the conclusion that a hysteresis effect exists in this combustion-chamber model. In reaching the transition from two-active-zones to one-sided-blowout from low feed rates, chamber operation moves from that represented by *Figure 12*(f) to that represented by *Figure 12*(a)—the high flow rate operation where the origin becomes an unstable solution. Once the transition occurs, re-light is accomplished by reducing the feed rate to a point where the one-sided-blowout solution is

below the blowout point of branch II. The feed rate where this critical level is reached is represented in *Figure 12*(e). Thus it may be concluded that, in this model, not only the blowout conditions but also the jet-flexibility (the slope of equation 11) and the ease of re-light are important chamber parameters.

In the discussion thus far nothing has been said either about the significance of the constants k_1 and k_2 of equations 11 and 12, or of how the chamber design affects them. The physical significance of these constants is amplified in terms of the jet parameters, chamber geometry and fuel composition in the Appendix.

Model showing effect of recirculation

Flow recirculation is another characteristic of combustion chambers to which the present technique of model analysis is adaptable. No allowance has been made thus far for combustion in the central zone, but a model in which such an allowance is made is probably in better agreement with the physical situation in a chamber fed by a jet of fuel–air mixture. In such a chamber the region of the jet near the base of the chamber aspirates burned gases from the surrounding region. These gases are replaced by reverse flow near the exit of the chamber. The gases in the recirculation zone appear experimentally to be moderately well mixed. To simplify further the model of this phenomenon the gases in the mainstream of the jet will also be treated as well-mixed.

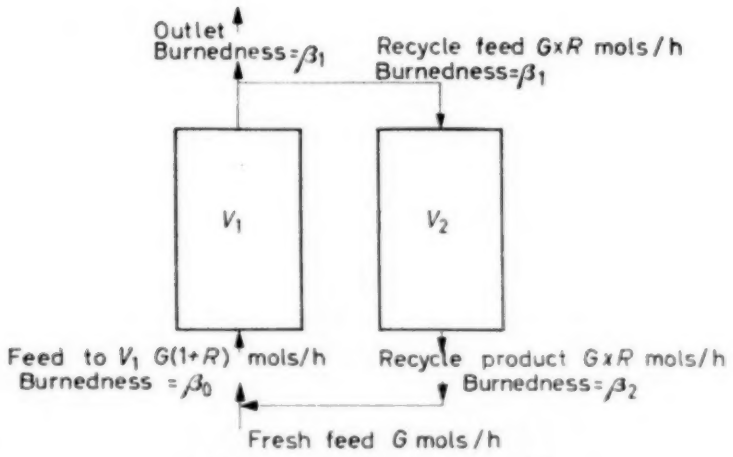

Figure 13. Recirculation model

The model of recirculation thus becomes two well-stirred volumes side by side (*Figure 13*). A portion of the partially burned products from the volume V_1 representing the central core is recycled through the second volume V_2 representing the two side recirculation zones, and back to V_1 again.

Applying the principles of well-stirred reactor theory discussed earlier it is possible to find the composition leaving either reactor, given the feed

rate, volume and entering composition. In this analysis the recirculation ratio is defined as

$$R = \frac{\text{molal recirculation rate to zone } V_2}{\text{molal fresh feed rate to zone } V_1}$$

By specifying a ratio V_2/V_1 and a recirculation ratio it is then possible to calculate the response of the model to increasing feed rates, although this is a trial-and-error procedure since account must be taken of the interaction of the two volumes. Since in a real combustor it is known that for a fixed geometry the flow patterns are relatively insensitive to Reynolds number, it is reasonable to calculate the curve of combustion efficiency versus feed rate of this recirculation model on the assumption that R, V_1 and V_2 do not change with feed rate.

This calculation has been carried out for a fixed V_2/V_1 ratio and fuel/air ratio using various recirculation ratios. Burnedness β, as a function of feed/total volume, is shown in *Figure 14* for a stoichiometric fuel/air ratio and a fixed V_2/V_1 ratio of two. If one were to assume a cylindrical chamber fed by a coaxial jet which reached the chamber walls at the outlet end, the central zone would be a cone and the recirculation volume the annulus between a cone and a cylinder; the ratio of V_2/V_1 for this geometry would be two. A sample calculation appears in *Figure 14*.

Several performance characteristics of this system should be noted. If the combustor is operating at a recirculation ratio of zero, the volume V_2 allowed for recirculation represents 'dead' space and the central core V_1 has only fresh unburned gases entering it. The central core, therefore, must be operating as a simple well-stirred zone without any additional assistance from the recirculated gases. The curve representing the behaviour of zero recirculation may be found by multiplying the curve for the simple well-stirred reactor by the fraction of the volume in the model which represents the active central core, i.e. by $V_1/(V_1+V_2)$; curve $R=0$ of *Figure 14*.

If, on the other hand, the recirculation ratio is infinite, the composition of both zones is the same and the performance becomes identical to that of the well-stirred reactor utilizing the total volume. Thus the curve for an infinite recirculation ratio is also the basic curve of well-stirred reactor performance, the one used to generate all of the other curves (curve $R=\infty$, *Figure 14*).

For recirculation ratios neither zero nor infinite significant interaction occurs between the central core and the recycle volume. This is illustrated by considering the relative contributions of each of the reactors to the total amount of combustion. Let the burnedness of the streams leaving reactors V_1 and V_2 be represented by β_1 and β_2 (the former also represents the burnedness of the gas entering V_2 and leaving the system); and let β_0 represent the burnedness of the gases fed to V_1, obtained by mixing gas of composition β_2 with fresh feed. The contribution to burnedness may be expressed quantitatively as the flow rate through the reactor times the

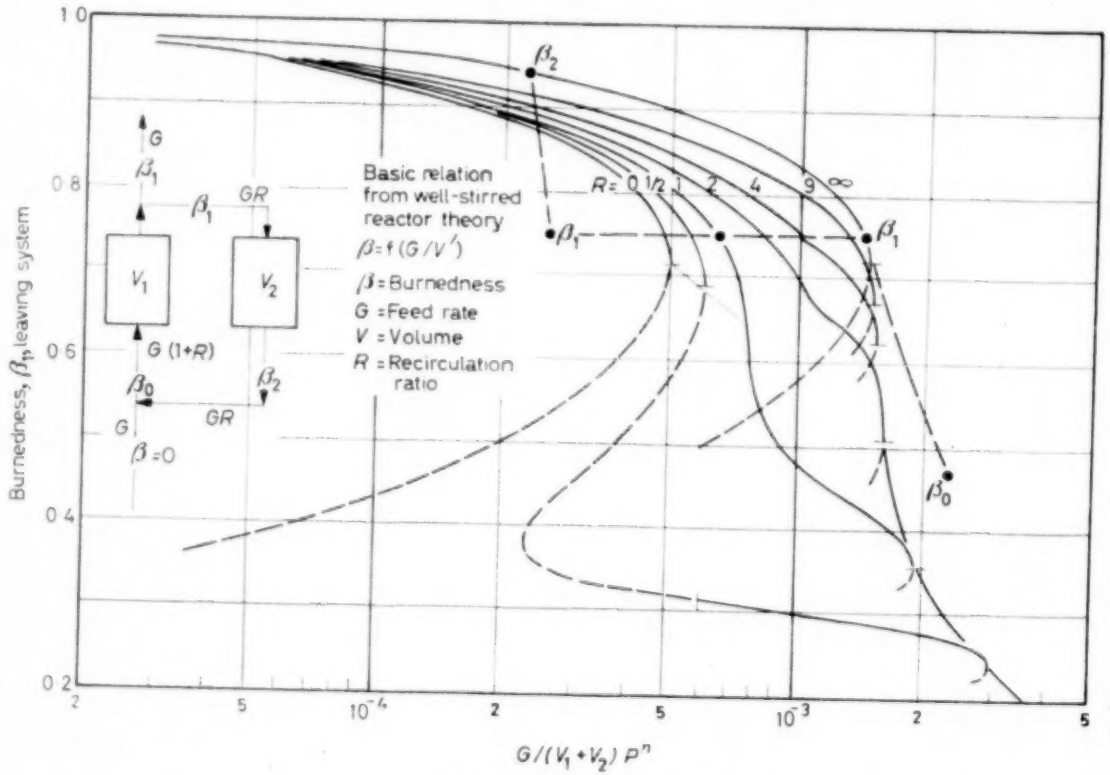

Figure 14. Effect of recycle in a combustion chamber model

Solution of example

Given:

$R = 1,\ \beta_1 = 0{\cdot}75,\ V_2 = 2V_1$

Find $G/(V_1+V_2)$

Assume $\beta_2 = 0{\cdot}94$

From material balance

$\beta_0 = \beta_2 R/(1+R) = 0{\cdot}47$

At $\beta = 0{\cdot}75,\ V_1'/G = 700$

Then

$$\frac{V_1}{G} = \frac{V_1'}{G}\frac{(\beta_1-\beta_0)}{\beta_1}(1+R) = 522$$

$$\frac{V_2}{G} = \frac{2V_1}{G} = 1\,044$$

$$\frac{V_2'}{G} = \frac{V_2}{G}\frac{\beta_2}{(\beta_2-\beta_1)}\frac{1}{R} = 4\,670$$

At $V_2'/G = 4\,670,\ \beta_2 = 0{\cdot}94$

Check assumed β_2 *value*

increase in burnedness in the reactor.

$$G \times \beta = G(1+R)(\beta_1 - \beta_0) + (G \times R)(\beta_2 - \beta_1)$$

$$\begin{bmatrix}\text{fresh feed rate to model}\end{bmatrix}\begin{bmatrix}\text{total change in burnedness in model}\end{bmatrix} = \begin{bmatrix}\text{feed rate to } V_1\end{bmatrix}\begin{bmatrix}\text{increase in burnedness in } V_1\end{bmatrix} + \begin{bmatrix}\text{feed rate to } V_2\end{bmatrix}\begin{bmatrix}\text{increase in burnedness in } V_2\end{bmatrix}$$

By dividing through by the total burning rate of the system, $G \times \beta_1$, two terms are obtained representing the fractional contribution, F, of each reactor

$$F_{V_1} = (1+R)(\beta_1 - \beta_0)/\beta_1$$

$$F_{V_2} = R(\beta_2 - \beta_1)/\beta_1$$

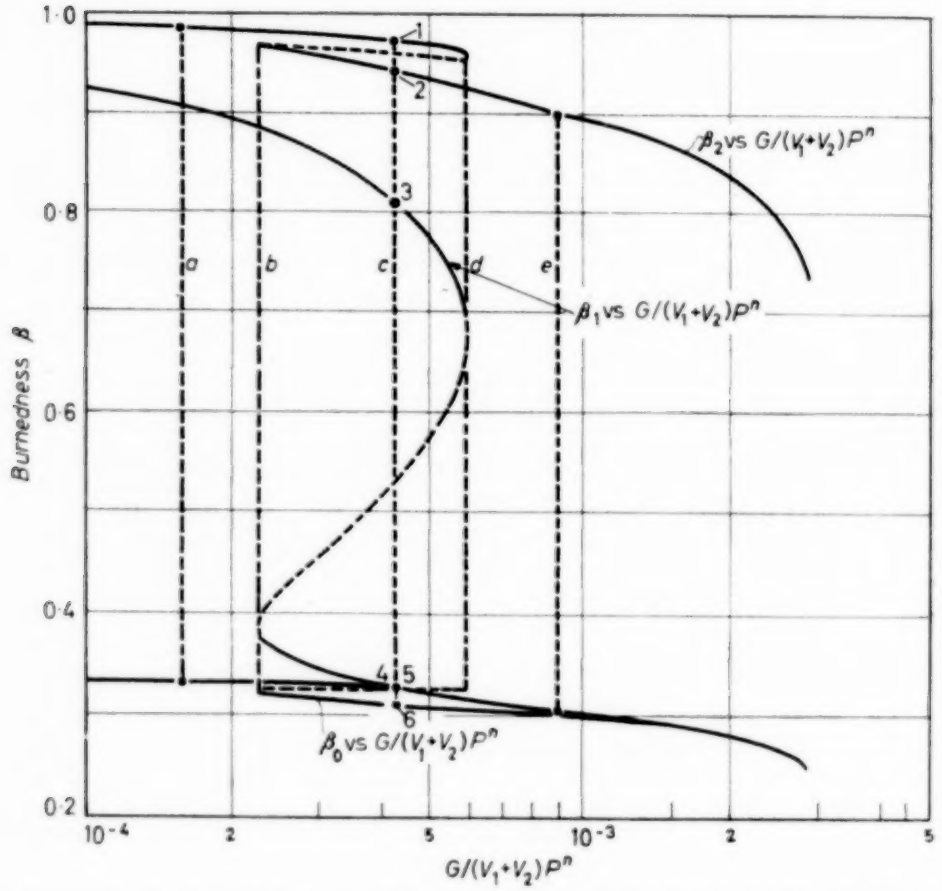

Figure 15. β_0, β_1 and β_2 versus $G/(V_1+V_2)P^n$ for recirculation model, with $R=\frac{1}{2}$

Choose an operating point corresponding to a moderately low feed rate, and consider the response of a fixed-volume reactor-pair to an increase in feed rate. *Figure 15* shows the behaviour of various points in the model for a recirculation ratio of a half and a V_2/V_1 ratio of two. Curve β_1 is the burnedness in the reactor V_1 and also the burnedness leaving the system:

curve β_2 is the burnedness in the recirculation zone; and curve β_0 is the composition of the feed to V_1 obtained by mixing fresh, unburned gases with recirculation products. At a low feed rate (represented by dotted line *a*) the feed material to V_2, of composition β_1, has a high burnedness, and there is very little burning remaining to be accomplished in reactor V_2. Under these conditions, the fractional utilization F_{V_2} of the recirculation zone is low, i.e. most of the burning occurs in V_1. At a higher feed rate represented by line *c*, the composition when approached from low flow rates corresponds to points 1, 3 and 5, and most of the burning still occurs in V_1; however, since the burnedness in V_1 decreases, F_{V_2} increases correspondingly. As the feed rate increases further past line *d* the central core becomes chilled, and a substantial blowout occurs, after which only the recycle volume is active, i.e. a residual flame. At feed rates beyond line *d* combustion occurs only along the lowest branch of the curve (corresponding to dotted line *e*). At these feed conditions practically no combustion occurs in the central core and F_{V_2} is nearly unity.

If the flow rate is now decreased from this high level, the central core stays cold past line *d*, and at line *c* the compositions 2, 4 and 6 are reached; and when line *b* is reached, there is a sudden re-lighting of the central core. This hysteresis loop is the most interesting part of these models, since it is a potential source of a flickering flame. In this region the central core may light or blowout in response to small disturbances in operating conditions with very little change in the burnedness of V_2.

At higher recirculation ratios the behaviour is similar but because of the 'stirring' effect of higher recycling the ratio of the fractional contribution of the two volumes, $[(\beta_2 - \beta_1)/(\beta_1 - \beta_0)] \times [R/(1+R)]$, approaches unity for a wider range of feed rates. As *Figure 14* indicates, the undercut of the curve of β_1 disappears (at $R \simeq 1$) as the recycle ratio is increased; with further increase, the inflection in the curve becomes less pronounced and finally disappears.

Model showing effect of non-uniform fuel/air ratio

Another problem of interest is that of allowing for the effect of unequal fuel/air ratios in the various chamber zones. Such a condition would arise in a combustor where the fuel and air were injected separately into a moderately well-stirred system. A possible model of such a combustor is a variation of the above recirculation model in which only a portion of the fuel but all of the air is fed to the central core, and the remainder of the fuel is fed to the recirculation zone. This produces a richer mixture in the recycle volume than in the central core. The one additional variable required may be thought of as either the fraction of original fuel introduced into the central core, or the fuel/air ratio of the recirculation volume. The former has the advantage of showing the limitations on the variations of fuel/air ratio in the recycle volume. The latter shows more directly the effect of the split in fuel feed. Since the fuel/air ratio in the central volume is the same as the overall fuel/air ratio, it will not be affected by this split.

The results of calculations made on this recirculation model are shown in *Figure 16* for an overall fuel/air ratio which is stoichiometric for consistency with the example of the previous model. Because of this condition any other fuel/air ratio in the recirculation volume can only be a detriment

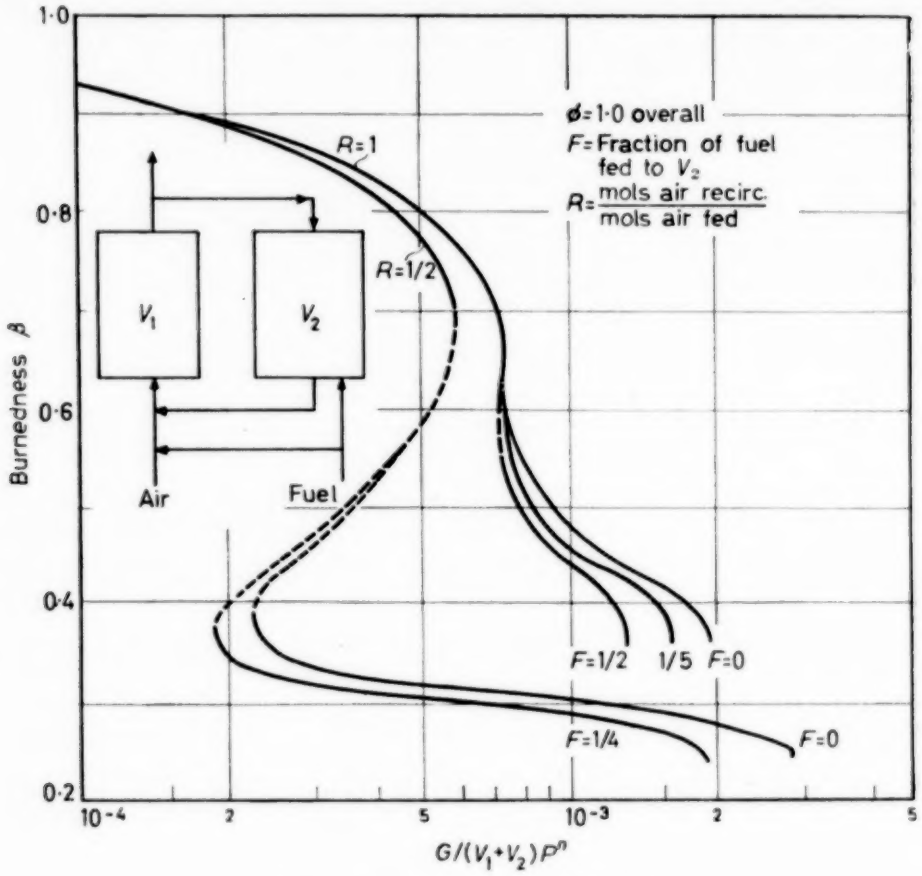

Figure 16. Effect of split-fuel feed

to the overall heat release rate, since the recycle zone must operate on less than the maximum efficiency curve. At low feed rates, this effect is of little consequence since the gases in the recirculation volume are essentially completely burned in either case. However, as the feed rate is increased the burnedness in the recirculation zone falls off and the effect of the lower efficiency curve appears.

If the chamber were operating with a lean overall fuel/air ratio and the fuel/air ratio in the recirculation zone were stoichiometric, the reverse situation would be expected. In this case the recirculation zone would be operating on a higher efficiency curve than the central core. In those feed-rate ranges in which the performance of the recirculation zone is important, the efficiency curve for an overall lean mixture with the fuel feed split to give a stoichiometric fuel/air ratio in the recirculation zone would be higher than for the case of feeding all the fuel into the central core.

DESCRIPTION OF EXPERIMENTAL WORK

To test whether conceptual models of the type presented here can be useful in predicting or explaining some of the phenomena of high-output combustors, an experimental programme is in progress. A two-dimensional chamber has been built which is fed by three slots along its floor and which has three opposing exit flues along the roof. In this chamber it has been possible to observe different combustion efficiencies in different portions of the chamber as well as a two-stability-limit phenomenon with an expansion of the stable zone. Since the chamber has as yet been fed only premixed air–fuel mixtures it has not yet been possible to observe any effects due to non-uniformity of fuel/air mixture ratio. Measurements of both blowout and combustion efficiency are being made. The blowout flow rates have averaged about 30 per cent of the blowout flow rates for the well-stirred reactors. Combustion efficiencies have been in the range of 70 to 75 per cent of theoretical oxygen consumption. A paper covering this experimental work will be presented later.

SUMMARY

This work has been undertaken to examine the implications of well-stirred reactor kinetics in the prediction of combustion chamber performance. It has been assumed that the gross performance characteristics of a combustion chamber can be simulated by models built up from interacting well-stirred reactor elements. Three different models have been examined analytically showing: (*1*) the effect of pressure interaction, (*2*) the effect of recirculation interaction, and (*3*) the effect of a non-uniform distribution of fuel/air ratio. These models have exhibited discontinuities and instability phenomena which parallel those found in an experimental programme now in progress. The results of the experimental programme thus far indicate that models based on simple combinations of well-stirred reactors are useful in analysing high-output combustion chamber performance.

This work was sponsored by Project Squid which is jointly supported by the Office of Naval Research, the Office of Scientific Research (Air Force) and the Office of Ordnance Research (Army) under Contract No. N6–ori–105, Task Order III. Reproduction in full or in part is permitted for any purpose of the United States Government.

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Cambridge, Mass.

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The appendix to this paper commences on page 32.

APPENDIX

Factors affecting the constants of equations 11 and 12

In any chamber which has a pressure difference transverse to the flow direction of a jet, a deflection of the jet centreline will be found. This deflection would be expected to be a function of the ratio of the pressure-area force and the jet-momentum force and, assuming dimensional similitude, this function may be expressed

$$\Delta y_r = \phi(\Delta P_r, x_r) \qquad \ldots . [13]$$

where $\Delta y_r = \Delta y / y_N$, $x_r = x / y_N$ and $P_r = P / \rho_N U_N^2$, when y_N = nozzle width, U_N = nozzle velocity, ρ_N nozzle density, ΔP = the difference in pressure on the two sides of the jet averaged from the nozzle to the height x above the nozzle, and Δy = deflection at the height x of the jet centreline. The change in volume, $V - V_o$, for either side may be computed by integration of the deflection of the jet over the height h of the chamber

$$V - V_o = w \int_0^h \Delta y \, dx = w y_0^2 \int_0^{h_r} \Delta y_r \, dx_r$$

$$= w y_0^2 \int_0^{h_r} \phi(\Delta P_r, x_r) \, dx_r \qquad \ldots . [14]$$

This reduces to

$$\tfrac{1}{2}(V_a - V_b) = w y_0^2 \Phi(\Delta P_r^*, h_r) \qquad \ldots . [15]$$

where ΔP_r^* is the reduced pressure difference averaged over the entire height and w is the width of the two-dimensional jet. This may be compared with equation 11

$$\tfrac{1}{2}(V_a - V_b) = k_1 (P_a - P_b) \qquad \ldots . [11]$$

To be in conformity with it, i.e. to make displacement proportional to ΔP, equation 15 must be of the form

$$\tfrac{1}{2}(V_a - V_b) = w y_0^2 (P_{ar} - P_{br}) F(h_r) \qquad \ldots . [16]$$

This equation may be rewritten

$$\frac{V_a - V_b}{V_a + V_b} = \frac{2 w y_0^2}{V_a + V_b} (\Delta P_r^*) F(h_r) \qquad \ldots . [17]$$

Each of the recirculation zones is postulated to be fed by an eddy diffusional process. This feed rate may be expressed in terms of an average outward velocity, U_o, which is applicable to the entire interface between the jet mainstream and the recirculation zone

$$U_o = a U_N \qquad \ldots . [18]$$

Using this outward velocity the outward momentum flux can be evaluated

$$\dot{M}_o = \rho_o U_o^2 = a^2 \rho_o U_N^2 \qquad \ldots . [19]$$

By applying a material balance, the gases entering the recirculation zone must all leave the recirculation zone

$$\dot{P_o U_o} = \rho_i U_i \qquad \ldots . [20]$$

The inward momentum flux is then

$$\dot{M}_i = \rho_i U_i^2 = (\rho_o U_o^2)(\rho_o/\rho_i) = a^2 (\rho_o U_N^2)(\rho_o/\rho_i) \qquad \ldots . [21]$$

Hence the net momentum flux crossing the boundary is

$$\Delta \dot{M} = a^2 \rho_o U_N^2 (\rho_o/\rho_i - 1) \qquad \ldots . [22]$$

and for two zones the pressure difference between them may be calculated, assuming there is negligible temperature rise in the jet mainstream, by the equation

$$P_a - P_b = a^2 \rho_N U_N^2 (T_a/T_N - T_b/T_N) \qquad \ldots . [23]$$

Now by an energy balance

$$T/T_N = \beta (T_{af}/T_N - 1) + 1 \qquad \ldots . [24]$$

Hence

$$\Delta P_r = a^2 (T_{af}/T_N - 1)(\beta_a - \beta_b) \qquad \ldots . [25]$$

which compares with

$$\Delta P = k_2 (\beta_a - \beta_b) \qquad \ldots . [12]$$

If *Figure 12* is now replotted using coordinates of $(V_a - V_b)/(V_a + V_b)$ and $(\beta_a - \beta_b)$, then the branches I and II, representing the relative performance of each side, are functions only of the total volume/feed ratio of the chamber. The jet deflection is related to the burnedness difference by combining equations 17 and 25

$$(V_a - V_b) = \left[a^2 \left(\frac{T_{af}}{T_N} - 1 \right) \frac{2 w y_o^2}{V_a + V_b} (h_r) \right] (\beta_a - \beta_b) \qquad \ldots . [26]$$

The coefficient of $(\beta_a - \beta_b)$ is the volume change produced by jet movement per unit difference in burnedness of the two sides, and may be referred to as jet sensitivity. The sensitivity of the jet may be increased by:

(*1*) increasing the jet spreading angle (a^2)

(2) increasing the height/nozzle width of the chamber

$$[2 w y_o^2/(V_a - V_b)](h_r)$$

(*3*) varying the feed composition or temperature to increase the term $(T_{af}/T_N - 1)$.

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The Variation with Temperature of the Explosibility Characteristics of Coal Dust Clouds using Electric Spark Ignition

D. L. CARPENTER and D. R. DAVIES

The variation with temperature of one explosibility characteristic, the minimum spark energy required for ignition, has been investigated with dust clouds of a selected range of South Wales and English coals. The existence has been revealed of an upper critical temperature beyond which ignition by electric spark becomes impossible with the apparatus used. The variation of the critical temperature values with the oxygen content of the dispersion medium obtained experimentally has proved, fairly conclusively, that the effect is due to the decreased oxygen concentration in the explosion chamber at the higher temperatures.

IN an effort to extend the range of coals which can be used in the manufacture of smokeless fuels the National Coal Board have developed fluidization processes wherein the caking and swelling tendencies of certain coals are reduced by mild oxidation. G. I. JENKINS[1] has described such a process where a bed of coal dust contained in a steel tower and maintained at temperatures of the order of 300°C is fluidized by a gas containing sufficient oxygen to effect the required oxidation. S. C. BLACKTIN and H. ROBINSON[2] have shown that under certain conditions voltages of up to 18 kV can be induced by a coal dust laden stream of air on to a metal surface. These authors were able to ignite inflammable gas–air mixtures with sparks derived from the induced charge on an insulated steel pipe. It is conceivable then that under suitable conditions an electrostatic discharge could be created in a coal dust cloud.

While there is considerable published information available as to the electrostatic discharge energy necessary for the ignition, at atmospheric temperatures, of the dust clouds of various substances including coal little information can be found concerning the effect of temperature on the minimum ignition energy. It was expected that for given conditions of pressure and oxygen concentration of the dust cloud the minimum ignition energy required would decrease with increasing dust cloud temperature thus enabling the hazard associated with any given set of conditions to be estimated. A plot of minimum ignition energy against dust cloud temperature would presumably show a continual decrease of ignition energy with increase in temperature up to temperatures at which the energy required for ignition would be very small. Extrapolation of the curve to meet the zero energy axis would give a temperature at which, theoretically, ignition could be obtained with a minute discharge energy. This temperature would then be the temperature at which spontaneous ignition of the coal dust

particles could be expected. The estimation of this hazard was the object of the investigation described below.

A knowledge of the capacitance and voltage to which a condenser is charged prior to its discharge across a spark gap defines the energy released in the discharge circuit, most of which appears in the spark discharge. Thus the values of the capacitance and voltage of the discharging condenser define the energy dissipated in the spark discharge but it does not follow necessarily that spark discharges of equal energy will have the same incendivity. In order to standardize the experimental procedure described below it was essential that for any given condenser capacitance and voltage the discharge circuit conditions were such that maximum spark incendivity was obtained. Any variations of minimum ignition energy due to variation of spark incendivity, with subsequent under-estimation of explosion hazard, would then be avoided.

EXPERIMENTAL PROCEDURE

The object of the investigation was to obtain information on the variation with temperature of the minimum energies required to effect ignition by electric sparks of a selected range of South Wales and English coals. The results obtained would, of course, refer to dusts of a given size and concentration dispersed by a gaseous medium of known oxygen concentration when both dust and dispersion medium had been brought to a specified temperature. To ensure reproducibility of results it was necessary that, for a given energy dissipation, the spark discharge used was of maximum incendivity. The coals used were limited by their ignition sensitivity to those containing more than 15 per cent volatile matter (d.a.f.) and to obtain maximum dispersion the coals were ground to pass through a 300 B.S. sieve. To avoid possible variation in chemical composition between the various sieve fractions of a coal dust the whole of each coal sample was ground mechanically until it passed through the 300 B.S. sieve and was then mixed thoroughly before use.

Apparatus

A sectional drawing of the apparatus finally developed is shown in *Figure 1*. The explosion chamber L, a mild steel cylinder 7 in. long and of volume 16·8 in^3 was closed at the base by an adaptor G screwthreaded into a circular steel baseplate H. The explosion chamber which was positioned rigidly inside the steel furnace casing was closed by a brass lid machined to give a close fit and held firmly in position by the clamps B_1, B_2. The furnace was heated electrically by the Nichrome winding W, heat loss being minimized by packing the outer casing D with asbestos wool. The two coils S_1, S_2 were formed from separate 8 ft lengths of $\frac{1}{4}$ in. copper tubing, one coil serving as a preheating chamber for the gas used to disperse the dust while the other coil could be used for preheating the gaseous medium passed through the explosion chamber to displace the air. This flushing of the explosion vessel would be required when dispersion media other than air were being used. The adaptor G and baseplate H were drilled to take a pair of concentric cylinders which were terminated by the

hemispherical cups Y and Z. The dispersion gas was introduced through the inner cylinder and was deflected downwards by the dispersion cone X onto the coal dust contained in the cup Y. If flushing of the explosion chamber was necessary the flushing gas was admitted to the annular space

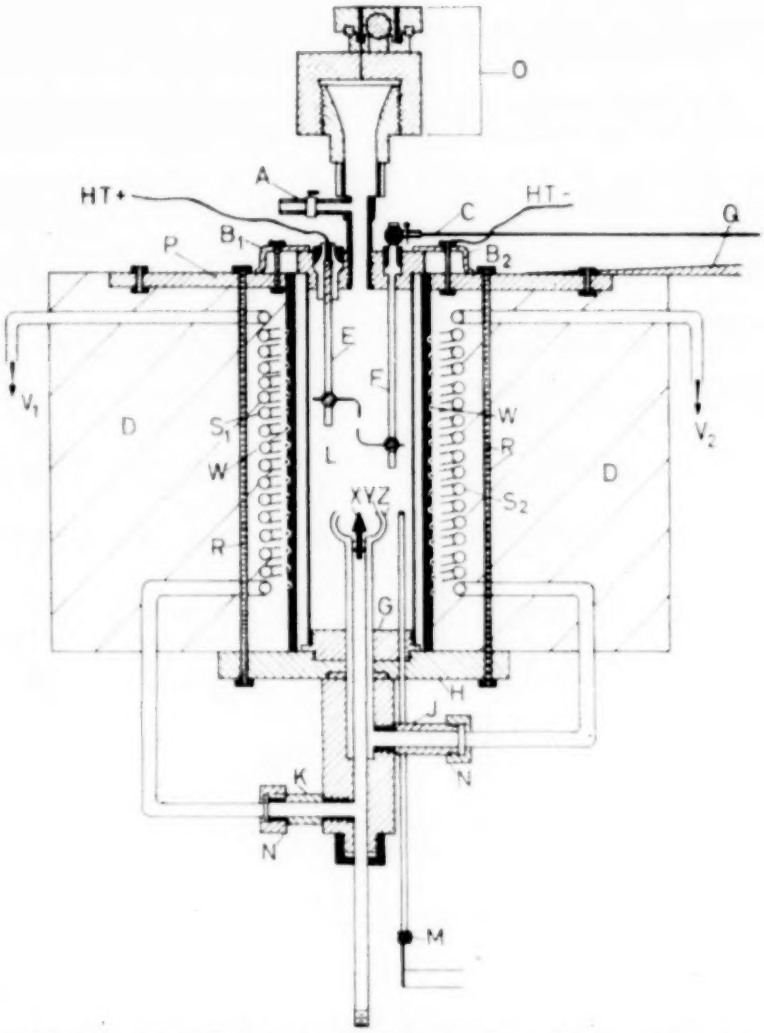

Figure 1. Detailed sectional diagram of explosion apparatus. Approximately ¼ full size

between the two cylinders leaving the chamber by the gas tap A. The explosion vessel temperature was measured by a chromel–alumel thermocouple M, the junction of which is positioned near the edge of the dispersion cup as shown. Exploration of the explosion chamber with a calibrated thermocouple had shown that the variation in temperature throughout the chamber was not more than 4°C at the highest temperatures used. The brass lid was drilled to take the optical pressure indicating assembly O together with the gas tap A which was opened during the flushing operation. Explosion of coal dust clouds was shown as the deflection of a narrow beam of light along a vertical calibrated scale. The insulated high voltage

electrode E was fitted rigidly into the brass lid while the earthed electrode F could be rotated about a vertical axis by the solenoid operated arm C. Before operation of the solenoid gap relay the gap between the electrodes was greater than the breakdown distance for the voltage used whereas actuation of the solenoid caused the earthed electrode to rotate so that it approached to within sparking distance of the insulated electrode. The electrode holders were stainless steel rods of 0·185 in. diameter to which were attached the 0·060 in. diameter stainless steel electrodes. The explosion chamber could be flushed by passing the gas through a control valve, then a non-return valve V_1 and one of the preheating coils, S_1, the rate of flushing being measured by a flowmeter. The dispersion gas supply, also valve controlled, passed through a reservoir and on to a solenoid operated gas valve. From the gas valve it entered the explosion chamber through a non-return valve V_2 and the second of the preheating coils, S_2.

To obtain optimum ignition conditions it was necessary to coordinate the dust dispersion and the passage of the spark discharge so that the spark occurred when the dispersed dust was in its most uniformly distributed state. The electrical apparatus used for the generation of the spark discharge and the synchronization of dust dispersion and spark discharge are illustrated diagrammatically in *Figure 2*.

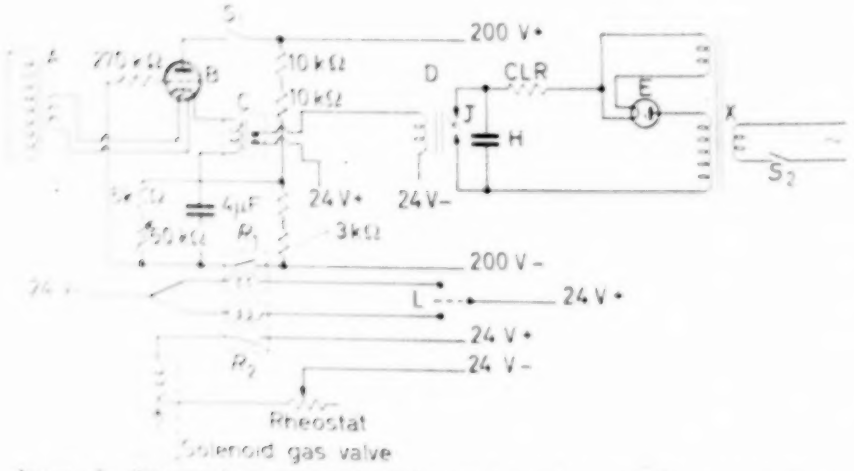

Figure 2. Circuit diagram of the delay and spark generating apparatus used in determination of minimum ignition energies

When the solenoid gap relay operated, the condenser H, having been charged by the diode-rectified output of the high voltage transformer X, discharged across the gap electrodes. The current limiting resistance CLR of 11 megohms was included to limit the influence of the transformer output on the spark current during discharge. The condenser was charged relatively slowly through this high resistance and then during discharge the resistance ensured that the current supplied to the gap from the transformer was small enough to have no effect on the spark characteristics. The fact that the time constant of the condenser charging circuit was appreciable meant that single spark discharges were produced requiring, therefore, correct synchronization with the dispersion of the coal dust.

Preliminary work was carried out on the reservoir pressure which would give most uniform distribution of the dust and a reservoir gauge pressure of 17 in. of mercury was finally adopted and used in all subsequent tests. The small deflection of the beam of reflected light produced by the entry of the dispersion gas into the explosion vessel was taken into account in deciding on the minimum deflection indicative of explosion. Further work was necessary to obtain the correct coordination between dust dispersion and spark discharge, while the weight of coal dust which would ensure the explosion of the dusts of as many coals as possible was found to be 0·1 g.

Character of the discharge

In view of the possible practical application of the results it was necessary to find the form of discharge most effective in the ignition of coal dust clouds. A. R. BOYLE and F. J. LLEWELLYN[3, 4] found that, with certain dusts, the insertion of a resistance into the discharge path increased the incendivity of the discharge. Coal dust clouds were not investigated and the only reported results are those of D. L. CARPENTER[5] who found that with sparks of moderate energy the effect of added resistance was negligible but that the insertion of an inductance into the discharge circuit definitely increased the incendivity. It should be pointed out, however, that Carpenter used a continuous spark generator the discharging condenser (0·0005 microfarad) being connected directly across the 8 kV output of a high voltage transformer, no attempt being made to obtain a unidirectional discharge.

The effect of addition of resistance to the discharge circuit shown in *Figure 2* was then investigated. The overall result of these tests was that for both large and small capacitance condensers, charged to the same voltage and tested with dispersions of the same coal dust, the addition of resistance did not produce increased incendivity—in fact a marked decrease in incendivity was observed with the larger discharging capacitances. The introduction of inductance also failed to improve spark incendivity even though the discharge increased in volume and appeared to be 'hotter'. It was assumed therefore that the lowest minimum ignition energies would be recorded using the direct capacitance discharge. Accordingly, the discharge circuit illustrated in *Figure 2* was used throughout the investigation.

Effect of temperature on sparking distance

For tests at atmospheric temperature the electrodes were positioned in their holders so that the gap width in the open position was greater than the breakdown distance of the condenser voltage. The condenser could thus be charged to the full transformer output voltage and remain charged until operation of the solenoid gap relay brought the electrodes within sparking distance. To minimize the delay between operation of the solenoid relay and passage of the spark the gap width in the open position was set to be only slightly greater than the breakdown distance. When tests at higher temperatures were attempted it was found that the open position gap width used at atmospheric temperature was unsuitable due to the effect of

electrode E was fitted rigidly into the brass lid while the earthed electrode F could be rotated about a vertical axis by the solenoid operated arm C. Before operation of the solenoid gap relay the gap between the electrodes was greater than the breakdown distance for the voltage used whereas activation of the solenoid caused the earthed electrode to rotate so that it approached to within sparking distance of the insulated electrode. The electrode holders were stainless steel rods of 0·185 in. diameter to which were attached the 0·060 in. diameter stainless steel electrodes. The explosion chamber could be flushed by passing the gas through a control valve, then a non-return valve V_1 and one of the preheating coils, S_1, the rate of flushing being measured by a flowmeter. The dispersion gas supply, also valve controlled, passed through a reservoir and on to a solenoid operated gas valve. From the gas valve it entered the explosion chamber through a non-return valve V_2 and the second of the preheating coils, S_2.

To obtain optimum ignition conditions it was necessary to coordinate the dust dispersion and the passage of the spark discharge so that the spark occurred when the dispersed dust was in its most uniformly distributed state. The electrical apparatus used for the generation of the spark discharge and the synchronization of dust dispersion and spark discharge are illustrated diagrammatically in *Figure 2*.

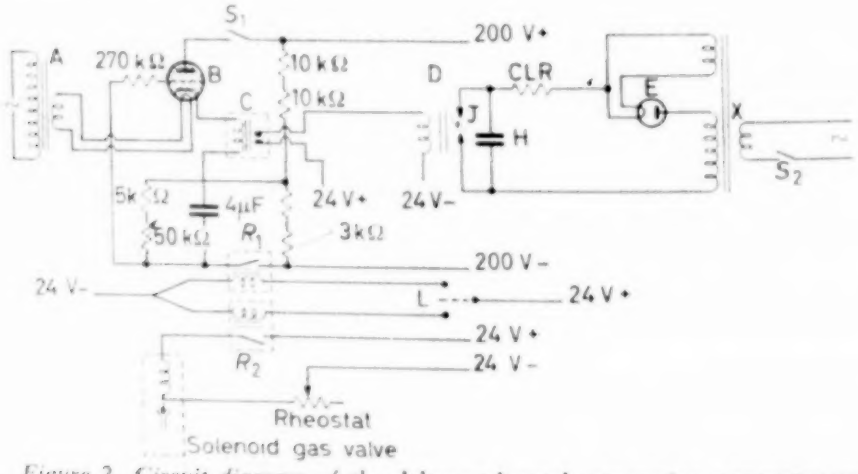

Figure 2. Circuit diagram of the delay and spark generating apparatus used in determination of minimum ignition energies

When the solenoid gap relay operated, the condenser H, having been charged by the diode-rectified output of the high voltage transformer X, discharged across the gap electrodes. The current limiting resistance CLR of 11 megohms was included to limit the influence of the transformer output on the spark current during discharge. The condenser was charged relatively slowly through this high resistance and then during discharge the resistance ensured that the current supplied to the gap from the transformer was small enough to have no effect on the spark characteristics. The fact that the time constant of the condenser charging circuit was appreciable meant that single spark discharges were produced requiring, therefore, correct synchronization with the dispersion of the coal dust.

Preliminary work was carried out on the reservoir pressure which would give most uniform distribution of the dust and a reservoir gauge pressure of 17 in. of mercury was finally adopted and used in all subsequent tests. The small deflection of the beam of reflected light produced by the entry of the dispersion gas into the explosion vessel was taken into account in deciding on the minimum deflection indicative of explosion. Further work was necessary to obtain the correct coordination between dust dispersion and spark discharge, while the weight of coal dust which would ensure the explosion of the dusts of as many coals as possible was found to be 0·1 g.

Character of the discharge

In view of the possible practical application of the results it was necessary to find the form of discharge most effective in the ignition of coal dust clouds. A. R. BOYLE and F. J. LLEWELLYN[3, 4] found that, with certain dusts, the insertion of a resistance into the discharge path increased the incendivity of the discharge. Coal dust clouds were not investigated and the only reported results are those of D. L. CARPENTER[5] who found that with sparks of moderate energy the effect of added resistance was negligible but that the insertion of an inductance into the discharge circuit definitely increased the incendivity. It should be pointed out, however, that Carpenter used a continuous spark generator the discharging condenser (0·0005 microfarad) being connected directly across the 8 kV output of a high voltage transformer, no attempt being made to obtain a unidirectional discharge.

The effect of addition of resistance to the discharge circuit shown in *Figure 2* was then investigated. The overall result of these tests was that for both large and small capacitance condensers, charged to the same voltage and tested with dispersions of the same coal dust, the addition of resistance did not produce increased incendivity—in fact a marked decrease in incendivity was observed with the larger discharging capacitances. The introduction of inductance also failed to improve spark incendivity even though the discharge increased in volume and appeared to be 'hotter'. It was assumed therefore that the lowest minimum ignition energies would be recorded using the direct capacitance discharge. Accordingly, the discharge circuit illustrated in *Figure 2* was used throughout the investigation.

Effect of temperature on sparking distance

For tests at atmospheric temperature the electrodes were positioned in their holders so that the gap width in the open position was greater than the breakdown distance of the condenser voltage. The condenser could thus be charged to the full transformer output voltage and remain charged until operation of the solenoid gap relay brought the electrodes within sparking distance. To minimize the delay between operation of the solenoid relay and passage of the spark the gap width in the open position was set to be only slightly greater than the breakdown distance. When tests at higher temperatures were attempted it was found that the open position gap width used at atmospheric temperature was unsuitable due to the effect of

temperature on the breakdown potential of the gas in the explosion chamber. The effect was so pronounced that sparking occurred at the open low temperature electrode setting when the temperature reached 150 to 200°C. To overcome this the open position gap width was increased progressively with increase in test temperature. This ensured that the condenser voltage at which discharge occurred was maintained at the maximum value even though the possible influence of variation of sparking distance on spark incendivity had been introduced.

Effect of temperature on minimum spark ignition energy of coal dust clouds using air dispersion

Standardization of procedure—Preliminary tests were made at various temperatures in order to find the procedure and condition variables which affected the reproducibility of results. The test procedure consisted of first adjusting the furnace temperature so that it remained constant at the value required. The 0·1 g quantity of −300 B.S. sieve coal dust was then placed in the dispersion cup which could be raised to the mouth of the explosion cylinder for this purpose. The dispersion cup was lowered to the correct position and the brass lid and attachments reassembled. The high voltage transformer was then energized and the dispersion gas reservoir filled to a gauge pressure of 17 in. of mercury. A few minutes were then allowed for the condenser to reach the transformer voltage and for the dust and explosion atmosphere to reach the furnace temperature. The appropriate switches in the synchronizing circuit (*Figure 2*) were then operated opening the solenoid gas valve to disperse the dust and causing the solenoid gap relay to initiate a spark discharge after a predetermined delay. These initial tests showed that the period for which the coal dust remained in the explosion chamber before dispersion and spark discharge had a marked influence on the result obtained. Consequently a fixed coal dust 'residence time' of three minutes was adopted. Constant dispersion conditions were ensured by the use of a gauge to set the position of the dispersion cone relative to the dispersion cup.

Of the wide range of coals available many could not be ignited in air even with the highest capacitance condensers (0·3 microfarad) used at temperatures up to 300°C. The proximate analysis of the coals which could be used is shown in *Table 1*.

Table 1. Proximate analysis of suitable coals

Lab. No.	Coalfield	Air-dried coal			D.a.f. coal	
		Moisture	Ash	VM less moisture	Fixed carbon	VM
		%	%	%	%	%
K1	Kent	1·0	3·9	14·8	80·3	15·6
K2	Kent	0·8	3·2	19·0	77·0	19·5
SW1	S. Wales	0·8	2·3	21·6	75·3	22·3
SW2	S. Wales	1·7	5·8	28·3	64·2	30·6
SW3	S. Wales	1·2	4·1	29·5	65·2	31·2
NC1	Northumberland and Cumberland	1·5	1·5	32·8	64·2	33·8
NC2	Northumberland and Cumberland	2·9	3·3	33·7	60·1	35·9
NC3	Northumberland and Cumberland	3·1	3·3	36·7	56·9	39·5

The minimum energy required for ignition is given by the expression $\frac{1}{2}CV^2$ where V is the voltage to which the condenser is charged, C is the highest capacitance at which not one explosion in ten tests could be obtained and where further increase in capacitance would give at least one positive result from ten tests. Most of the dust remaining in the explosion cylinder was removed after each test by a jet of compressed air while the cylinder was cleaned thoroughly after every ten tests.

Figures 3 and *4* show the variation of minimum ignition energy with temperature for the dusts of seven coals. Since air was used as dispersion medium no flushing of the explosion chamber was necessary. At temperatures up to about 250°C the graphs show the expected decrease in ignition energy with increase in temperature and also that for a given temperature the minimum energy increases with increase in coal rank. For temperatures up to 350°C coal dusts of less than 19·0 per cent volatile matter (d.a.f.) could not be ignited when air-dispersed and temperatures greater than 100°C were necessary to effect the ignition of a coal dust of 19·5 per cent volatile matter. The surprising feature common to each graph is that at temperatures around 300°C the minimum ignition energy increases so rapidly with temperature that a temperature increase of a few degrees renders the dusts of each coal non-explosive with the maximum energy discharges used. At temperatures approaching 300°C it was found that the longer the coal dust was allowed to remain in the apparatus before dispersion and ignition, i.e. the greater the residence time, the greater the number of negative results obtained in a series of ten tests—hence the adoption of a constant residence time of three minutes.

The results obtained with each coal indicated that with the air-dispersed and spark-ignited dust clouds of all the seven coals tested a critical temperature existed in the region of 300°C, at which the explosibility of the dust cloud decreased rapidly with further increase in temperature. Possible explanations of this rather surprising effect include:

(*a*) The partial thermal decomposition of the coal dust before dispersion. Increase in residence time would accordingly decrease the explosibility.

(*b*) The formation of an oxygenated product between gaseous oxygen and the dust particles before dispersion. The formation of this complex would possibly decrease the oxygen reactivity of the dust particles and hence decrease their explosibility.

(*c*) The decrease of oxygen concentration in the explosion cylinder as a result of the oxidation of the coal sample during the residence period. The oxygen concentration and therefore the explosibility would decrease with increase in residence time and also with increase in weight of coal sample tested.

(*d*) The necessary increase of gap distance with increase in temperature to give a range of gap distances in which separation of the electrodes might produce a rapid decrease in spark incendivity.

(*e*) The decrease, at constant pressure, of oxygen concentration in moles/unit volume with increase in temperature. Since the dispersion gas

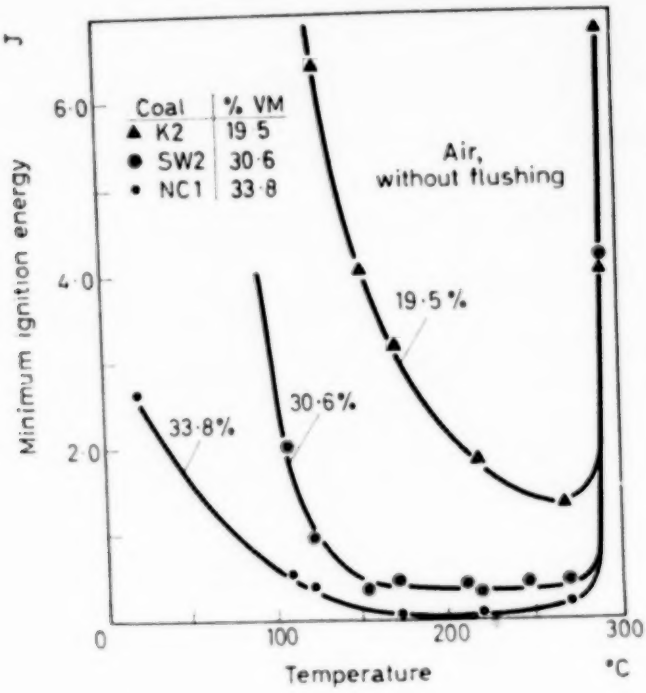

Figure 3

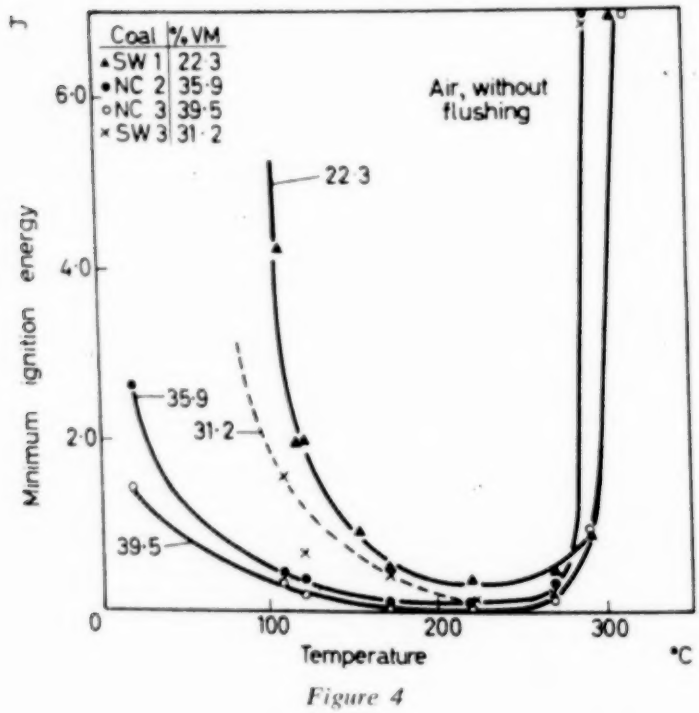

Figure 4

Figures 3 and 4. Variation of minimum ignition energy with temperature for a selected range of coals using air dispersion without prior flushing of explosion chamber

reservoir pressure is kept constant for all tests and the pressure in the explosion cylinder immediately before dispersion is atmospheric, then the pressure in the explosion cylinder after dust dispersion and at the moment of ignition is practically constant for all temperatures used. As the temperature increases, the actual concentration of oxygen molecules decreases even though the oxygen partial pressure remains constant due to the increase in kinetic energy of the molecules. The explosibility would increase at first with temperature increase due to the fact that at temperatures up to 250°C the oxygen concentration is still sufficient to allow the effect of temperature on reaction rate to be the dominant factor. When the temperature exceeds 250°C the availability of oxygen molecules for sustained reaction becomes increasingly important until, under these conditions, at a temperature of about 300°C the oxygen concentration is insufficient to support propagated combustion.

The explanation offered in (*a*) and probably that given in (*b*) may be ruled out by the following experimental observation. A 0·1 g quantity of a coal dust which had been tested repeatedly at 300°C and could not be ignited, was placed in the dispersion cup and allowed to remain in the reassembled apparatus for the normal period of three minutes. The furnace was then cooled through about 50°C and the dust dispersed and tested at the lower temperature. Ignition was obtained during each of several such tests. A further objection to reason (*b*) is that if the coal dust, after being held at 300°C for three minutes, is removed, cooled and then replaced in the dispersion cup, ignition was obtained, provided the test was carried out as quickly as possible after reassembly.

To check the explanation offered in (*d*) the apparatus would have to be modified to enable a fixed gap to be used. The work of P. G. GUEST[6], however, does not indicate that any rapid increase in ignition energy occurs with increase in gap width particularly with electrodes of small diameter. If, as explanation (*e*) suggests, the existence of a critical temperature is due to the decrease in oxygen concentration then change in the oxygen content of the medium should produce a change in the temperature at which the sudden increase in ignition energy occurs. Decrease in oxygen concentration of the dispersion medium should produce a decrease in the critical temperature. The variation of ignition energy with temperature was therefore studied using as dispersion medium an oxygen–nitrogen mixture containing 17 per cent oxygen. Since the dispersion medium was not air, flushing of the apparatus was necessary to ensure that all the air, present in the explosion cylinder after reassembly, was replaced by the 17 per cent oxygen mixture. The flow rate of flushing gas was adjusted so that during the normal residence period of three minutes analysis of the explosion chamber atmosphere revealed an oxygen content equal to that of the dispersion gas. In all other respects the test conditions and procedure used were identical with those employed with air dispersion tests. The variation obtained with the dusts of three coals is shown in *Figure 5*.

As might be expected decrease in the oxygen content of the dispersion medium decreases the explosibility of the coals at the lower temperatures

and in fact prevented the ignition of coals with less than 33·0 per cent volatile matter (d.a.f.). Even with the coals which could be ignited temperatures of more than 100°C were necessary to effect ignition with the

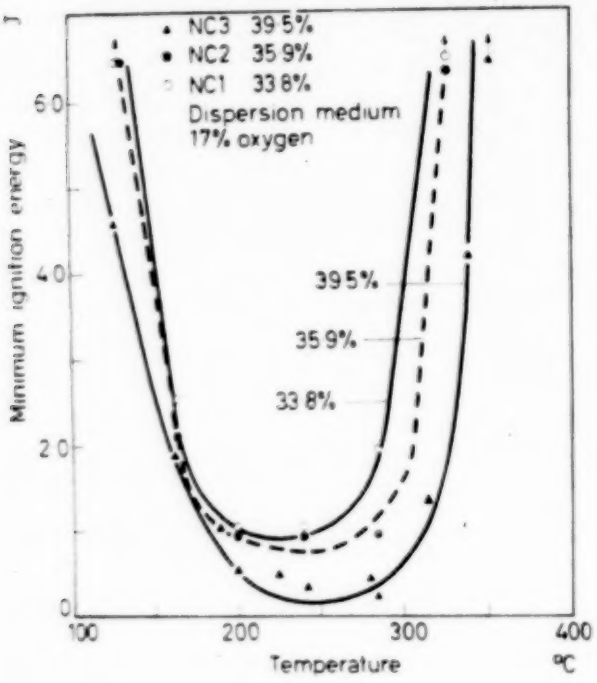

Figure 5. Variation of minimum ignition energy with temperature for three coals using a 17 per cent oxygen mixture as dispersion medium necessitating flushing of explosion chamber

highest energy sparks used. The pressures developed during these explosions were lower than those observed with the air-dispersed dusts and decreased with increase in temperature above 270°C. The graphs obtained with two coals in both air and the 17 per cent oxygen mixture are compared in *Figure 6*.

The critical temperatures of each of the three coals tested in the 17 per cent oxygen mixture are definitely higher than the corresponding values obtained using air dispersion. Whereas with air dispersion the dust of coal NC3 could not be ignited at temperatures above 315°C, tests with the 17 per cent oxygen mixture showed that the same coal could be ignited at temperatures up to 339°C. This result is of course the reverse of what was expected and further work was necessary either to justify or to eliminate the suggested influence of variation of oxygen concentration with temperature.

Effect of flushing explosion chamber on explosibility of coal dust clouds—The only difference in test conditions between the determinations of ignition energies using air dispersion and those in which the 17 per cent oxygen mixture was used was that flushing of the explosion chamber was not employed for the tests which used air dispersion. The variation of ignition energy with temperature using air dispersion was therefore investigated using a flushing rate identical with that adopted for the dispersion in 17 per cent oxygen mixtures. The variation of ignition energy with temperature

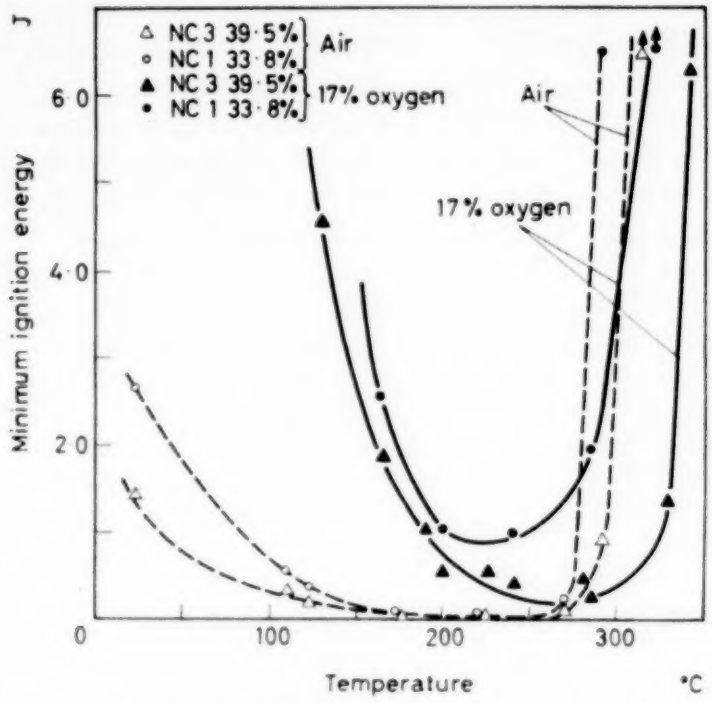

Figure 6. Comparison between variation of minimum ignition energy with temperature for two coals using an explosion atmosphere of: (a) *air without flushing, and* (b) *a 17 per cent oxygen mixture with flushing*

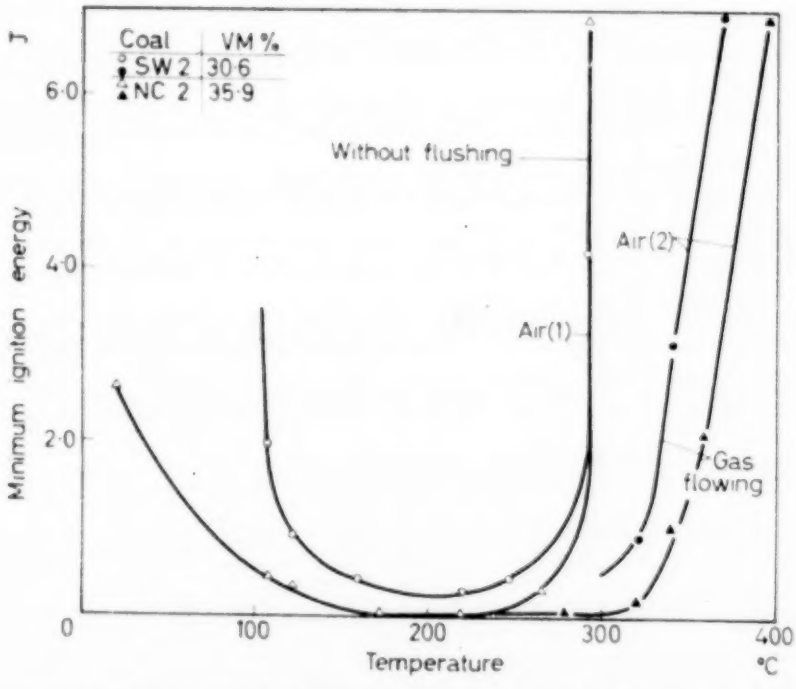

Figure 7. Effect of prior flushing of explosion chamber on variation of minimum ignition energy with temperature for two coals using air dispersion

obtained under these conditions is shown in *Figure 7* where it is compared with the graph obtained for air dispersion without flushing.

The graphs show that the flushing of the explosion cylinder with air prior to the tests has increased the critical temperature obtained previously with air dispersion by about 90°C. It is suggested that the increase in critical temperature is due to a combination of the following effects:

(*i*) The flushing air, even though its flowrate is not high, may not attain the temperature of the furnace during its passage through the preheating coil and explosion cylinder. The junction of the thermocouple, as seen in *Figure 1*, was positioned at the same level as the upper edge of the dispersion cup and consequently lay outside the path of the flushing gas. The temperature recorded by the thermocouple would not necessarily be the temperature of the gas passing through the explosion cylinder. As soon as flushing was discontinued the explosion cylinder outlet tap was closed and the dust dispersed immediately so that little time was available after flushing for the gas in the explosion cylinder to reach the furnace temperature.

(*ii*) Explanation (*c*) above suggests that the oxygen concentration in the explosion chamber may be reduced appreciably during the oxidation of the undispersed coal dust. Continuous renewal of the explosion atmosphere prior to dispersion would probably ensure a higher oxygen concentration in the explosion chamber at the moment of dust dispersion than that existing when flushing was not employed.

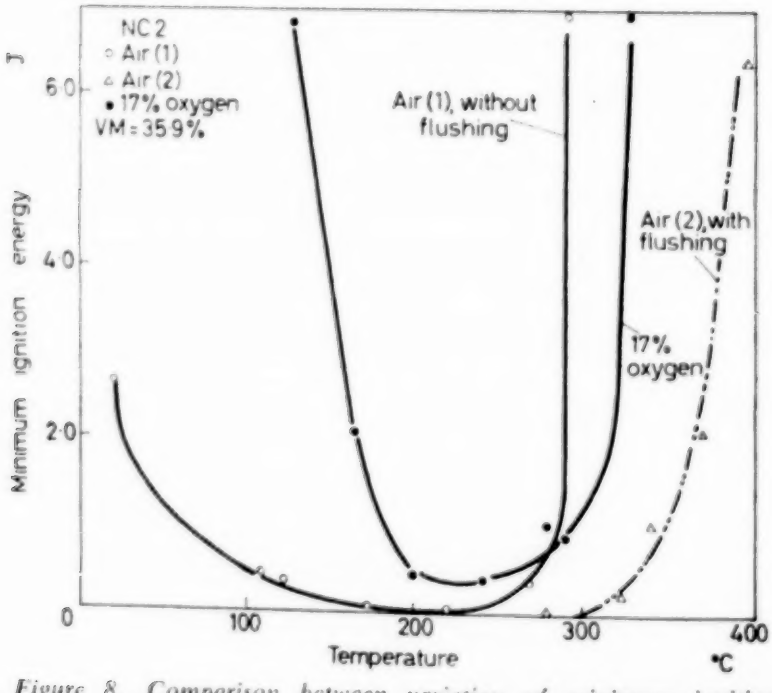

Figure 8. Comparison between variation of minimum ignition energy with temperature for one coal dispersed in: (a) *air without prior flushing,* (b) *air with flushing, and* (c) *a 17 per cent oxygen mixture*

The graphs shown in *Figure 7* are compared in *Figure 8* with the variation of ignition energy with temperature obtained using the 17 per cent oxygen mixture.

It can be seen from *Figure 8* that, provided the test conditions are identical, decrease of the oxygen content of the dispersion medium has the effect expected, decreasing the critical temperature at which a rapid decrease in explosibility occurs.

To obtain conclusive evidence regarding the importance of oxygen concentration in determining the upper critical ignition temperatures of coal dust clouds further tests were carried out using as dispersion medium an oxygen–nitrogen mixture containing 28 per cent oxygen. Preliminary tests at room temperature showed that when using the adopted flushing rate and flushing time of three minutes the explosion chamber atmosphere was replaced completely by the dispersion medium. The variation of ignition energy with temperature of the dusts of five coals ranging from 19·5 to 39·5 per cent volatile matter (d.a.f.) is shown graphically in *Figures 9* and *10*.

The temperature range over which ignition could be effected by spark discharges of moderate energy had been increased appreciably by the increase in the oxygen content of the dispersion medium. The upper critical temperatures now occur at values ranging from 375°C for the higher rank coals to 450°C for coals of lowest rank. It will also be noted that for each of the three different dispersion media used and for identical test conditions, the critical temperatures observed all increase with decrease in coal rank. Bearing in mind the fact that the lower rank coals are the more readily ignited it follows that for a given temperature the reaction rate will be greatest for the coals of lowest rank. Consequently the oxygen concentration will have to be further reduced (i.e. higher temperatures employed) in order to reduce the reaction rates to values below those required for propagated combustion. The graphs obtained with a coal of 35·9 per cent volatile matter (d.a.f.) in each of the three dispersion media used are compared in *Figure 11*.

The critical temperatures observed with this coal increase with increase in oxygen concentration and show fairly conclusively that the existence of a critical temperature is due to the fact that there is a limiting oxygen concentration below which ignition cannot be obtained with the highest spark energies employed.

The reduction of oxygen concentration to a critical value may have been brought about by either:

(*a*) the decrease in density of the dispersion medium with increase in temperature, or

(*b*) the increase, with increase in temperature, of the oxidation of the undispersed coal dust by the flushing gas prior to dispersion. The greater the rate of oxidation of the coal dust the lower will be the oxygen concentration in the explosion chamber at the moment of dust dispersion, or by a combination of (*a*) and (*b*).

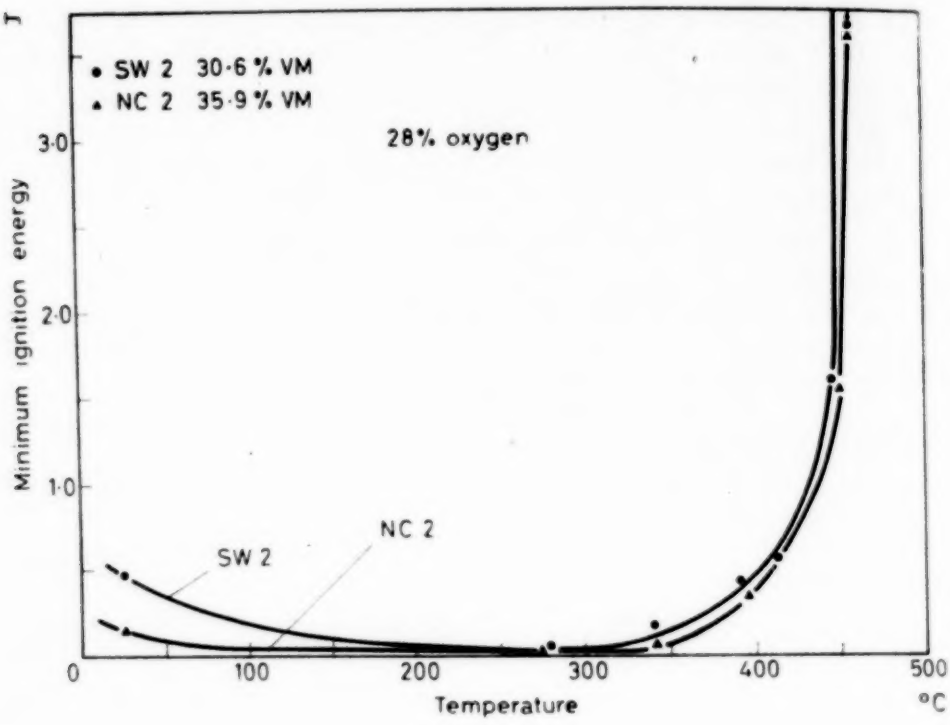

Figure 9

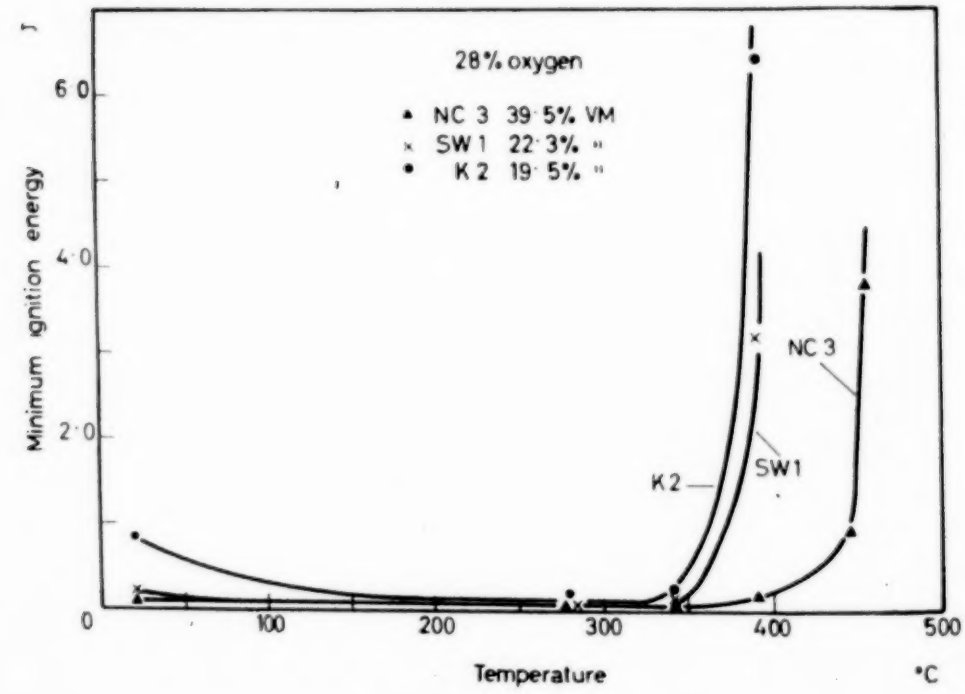

Figure 10

Figures 9 and 10. Variation of minimum ignition energy with temperature for five coals using a 28 per cent oxygen mixture as dispersion medium

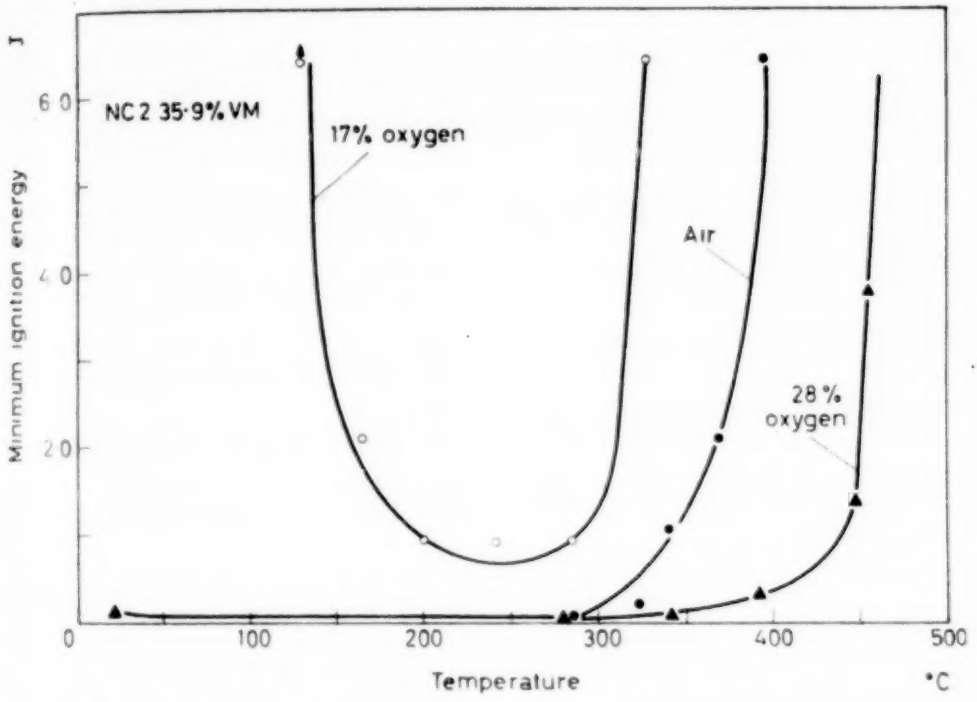

Figure 11. Variation of minimum ignition energy with temperature for one coal using identical test conditions and dispersion media of: (a) *a 17 per cent oxygen mixture,* (b) *air, and* (c) *a 28 per cent oxygen mixture*

The extent of the oxidation of the undispersed coal dust sample by the flushing gas was measured by passing air through the explosion chamber at the rate used during explosibility measurements and analysing the emergent gas for various explosion chamber temperatures. 0·1 g quantities of NC2 coal ground to pass through a 300 B.S. sieve and containing 35·9 per cent volatile matter (d.a.f.) were used. The measurement of minimum ignition energy of this coal dispersed in air with prior flushing of the explosion chamber showed an increase in ignition energy as the temperature increased above 275°C, ignition becoming impossible at a temperature of 375°C. At an explosion chamber temperature of 260°C analysis of the emergent flushing gas showed an oxygen content of 17·5 per cent while at 350°C the oxygen content decreased to 14·2 per cent. Further increase of temperature to 375°C caused a further decrease of oxygen content to 12·5 per cent while the carbon dioxide content increased from 1·0 per cent at 260°C to 4·2 per cent at 375°C. This rapid decrease in oxygen concentration in the explosion chamber with increase in temperature from 260°C to 375°C does suggest that oxidation of the undispersed coal dust may be an important factor. On the other hand the coal dust is dispersed by gas from the reservoir and preheating coils which will not have suffered any loss in oxygen content. Further, the coals which, for a given dispersion medium, show the highest critical temperatures are those of lowest rank (*Figure 10*). These coals being the more reactive would be expected to remove oxygen from the explosion atmosphere at a greater rate than higher rank coals and should therefore show lower critical temperatures. The

fact that, when flushing is not used, the explosibility of a given dust does decrease with increase in residence time and also with increase in the quantity of coal dust present in the explosion chamber does suggest, however, that oxidation of the undispersed coal dust may be responsible for the observed increase of ignition energy with temperature.

It is still possible, however, that the variation with temperature of the gap width at which discharge occurs may be at least partly responsible for the existence of a critical temperature. Increase in oxygen concentration could compensate for the decrease in spark incendivity accompanying the increase in sparking distance. Thus increase in oxygen content of the dispersion medium would allow lower spark incendivities (i.e. higher sparking distances or higher test temperatures) to be used before ignition again became impossible. The possible effect of sparking distance on discharge incendivity could be shown by carrying out the tests with a discharge circuit modified to enable fixed electrodes of constant gap width to be used.

VARIATION OF MINIMUM IGNITION ENERGY WITH TEMPERATURE OF AIR-DISPERSED COAL DUSTS USING FIXED ELECTRODES

The discharge circuit shown in *Figure 2* was replaced by an apparatus in which the spark was produced by the discharge of a high capacitance condenser, charged to 200 V, across the primary winding of an induction coil. The secondary winding of the coil, giving a peak output voltage of approximately 10 kV, was connected across the electrodes. The solenoid gap relay, shown in *Figure 2*, was discarded as both electrodes were rigidly positioned to ensure a constant gap width for all tests. Synchronization of dust dispersion and spark discharge was achieved using the apparatus employed by one of the authors (D.L.C.[3]) in the determination of the relative minimum explosive concentration of coal dust in air-dispersed clouds. Variation of ignition energy was obtained by the variation of condenser capacitance from 1 to 52 microfarads. The energy dissipated across the electrodes was assumed to be that stored in the condenser and expressed by $\frac{1}{2}CV^2$ where C denotes the capacitance used and $V = 200$ V. After preliminary work on the coordination of dust dispersion and spark discharge to obtain optimum ignition conditions the effect of variation of gap width was studied and finally gave a gap width of 0·30 in. as that producing the most incendive spark. Flushing was not used prior to the air dispersion of the coal dusts but all other test conditions remained unchanged.

Figures 12 and *13* show the comparison between the minimum ignition energy/temperature variation for each of two coals using air dispersion without flushing, the spark discharge being generated by first the direct capacitance discharge with a moving earthed electrode and secondly the induction coil spark discharged across a fixed gap width. The scale of the ignition energy coordinate has been enlarged to enable a close comparison to be made. These curves show marked similarity, the sudden increase in explosibility occurring at almost identical temperatures. This close similarity is a little surprising bearing in mind the very different

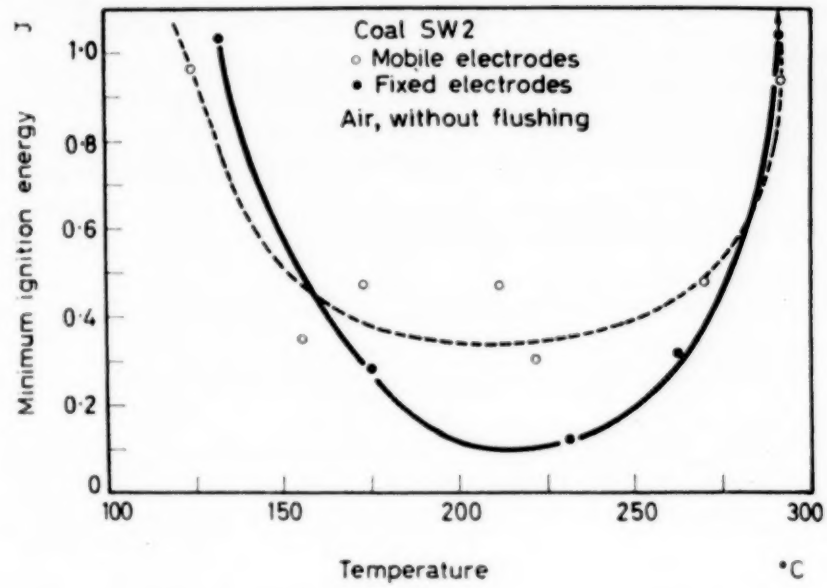

Figure 12

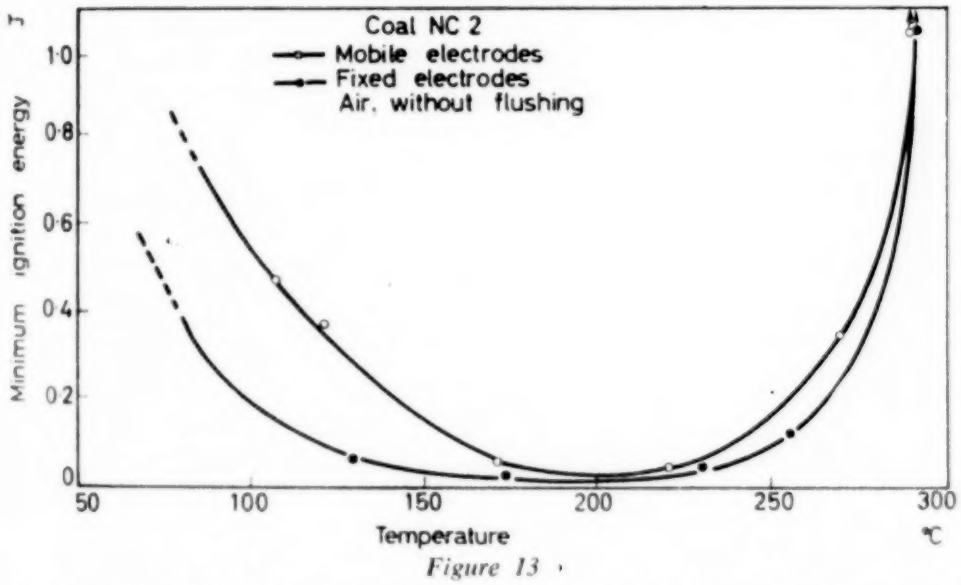

Figure 13

Figures 12 and 13. Comparison between variation of minimum ignition energy with temperature for each of two coals using spark discharges produced by: (a) direct condenser discharge across a varying gap distance, and (b) *the application of an induction coil output voltage across a fixed gap distance*

methods of spark generation and the change in gap conditions. It follows that any effect of sparking distance on incendivity may be eliminated as a possible explanation of the existence of an upper critical temperature.

SUMMARY

Ignition of coal dust clouds by direct condenser discharge

(A) *Air dispersion without flushing*—

(1) Only coals of volatile content greater than 19 per cent could be ignited.

(2) At temperatures below about 220°C the ease of ignition increased with decrease in rank and with increase in temperature. As the temperature was increased above 220°C the ignition energies began to increase slowly.

(3) For all the coals tested an upper limit of explosibility was observed, above which ignition could not be obtained with the highest energy sparks used. The value of the critical temperature, which was to some extent influenced by coal rank, lay in the range 280 to 310°C.

(4) Minimum ignition energies of less than 0·5 J were recorded in the temperature range 170° to 270°C for all coals with more than 22·0 per cent volatile matter. With coals of volatile matter content greater than 33·0 per cent a spark of this energy produced ignition at 108°C.

(B) *Dispersion by a 17 per cent oxygen mixture with flushing*—A reduction of the oxygen concentration in the explosion atmosphere from 20·9 per cent (air) to 17 per cent resulted in a marked decrease in the explosibility of all the coal dusts. Only coals of volatile content greater than 33 per cent could be ignited and then only at elevated temperatures. Minimum ignition energies of less than 0·5 J were confined to the coal of lowest rank (39·5 per cent volatile matter) which showed maximum explosibility over the temperature range 200° to 290°C with an upper critical temperature of 327°C. Higher spark energies were required for the ignition of coals of volatile matter contents 33·8 and 35·9 per cent, the temperature range over which ignition was possible being correspondingly narrower.

(C) *Air dispersion with flushing*—The flushing of the explosion vessel for air dispersion was found to have a marked effect on the upper critical temperatures effecting an increase from a value of 290° to 380°C for NC2 coal. That is, for identical test conditions, air dispersion produces higher critical temperatures than does dispersion by an oxygen–nitrogen mixture containing 17 per cent oxygen.

(D) *Dispersion by a 28 per cent oxygen mixture with flushing*—Increase in oxygen concentration to 28 per cent resulted in an appreciable increase in the explosibility of all the coal dusts. At atmospheric temperature minimum energies of less than 0·5 J were recorded for all the coals containing more than 22 per cent volatile matter. The critical temperatures were observed to be higher than those recorded using air dispersion, e.g. NC2 coal tested under identical conditions in each of the dispersion media containing 17·0, 20·9 and 28 per cent oxygen gave respectively critical temperatures of 325°, 380° and 450°C.

Ignition of coal dust clouds by induction coil sparks

For the two coals studied the minimum ignition energy/temperature variation was found to be practically independent of the nature of the spark discharge. Sparks produced by the direct discharge of condensers of various capacitances charged to 6·5 kV gave results almost identical with those recorded using the discharge obtained from the secondary of an induction coil when condensers of various high capacitances charged to 200 V were allowed to discharge through the primary winding of the coil.

CONCLUSIONS

The study of the minimum ignition energy/temperature relationships for the dusts of a number of coals dispersed in media of various oxygen concentrations has revealed the existence of an upper critical temperature beyond which ignition could not be obtained. The fact that, for identical test conditions, the critical temperature increases with increase in the oxygen content of the dispersion medium indicates fairly conclusively that the decrease of oxygen concentration in the explosion atmosphere is responsible. Other possible reasons for the existence of an upper critical temperature have been examined and disproved experimentally. The oxidation of the undispersed coal dust is certainly responsible for a decrease in oxygen concentration in the explosion chamber. The effect of decrease in oxygen density (moles/unit volume) in the explosion chamber with increase in temperature may also be an important factor in determining the variation of ignition energy with temperature. The relative importance of these two effects could only be assessed by measuring the ignition energy/temperature relationships under conditions in which no possible oxidation of the coal dust sample could occur prior to dispersion.

The critical temperatures observed have no absolute significance and will depend upon experimental conditions which apart from the oxygen concentration of the dispersion medium will include the quantity and fineness of the coal dust test sample and probably the volume of the explosion chamber. The results obtained do not permit any predictions to be made as to the fire and explosion hazard associated with dispersed clouds of any of the dusts tested. Temperature ranges can be given over which, for the conditions specified, the spark energy required for the ignition of the dust cloud is a minimum. The relative ignitibilities of the dust clouds of the various coals at temperatures below the critical values can also be assessed. Any attempt to predict the explosion hazard at temperatures near the critical values would be unwise, but it may be concluded from the experimental work described here that in a process such as the oxidation of fluidized coal particles the explosion hazard decreases appreciably as the oxidation proceeds.

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The Methyl Nitrite Decomposition Flame*

E. A. ARDEN and J. POWLING

The methyl nitrite decomposition flame has been studied at atmospheric pressure. The course of reaction has been followed through a flat flame by measuring the changes in gas composition and temperature. The burning velocity of the decomposition flame relative to the vapour at 200°C was 7·3 cm/s and the maximum temperature attained was about 1 100°C. The nitrite first decomposes thermoneutrally to nitric oxide, methanol and formaldehyde and subsequent exothermic reaction takes place in these products. Reaction does not go to completion, however, the reduction of nitric oxide, ceasing when the decomposition of methanol and formaldehyde is complete (about 40 per cent of the nitric oxide remains unchanged in the final products at atmospheric pressure) yet, whilst addition of nitric oxide to the nitrite entering the burner has a pronounced effect, extra formaldehyde and methanol have little influence. Water is the only major oxidation product. Auxiliary experiments on the propagation of flame in static mixtures contained in a heated tube have been made. A mixture of nitric oxide, methanol and formaldehyde such as is found in the nitrite flame will not ignite without a sensitizer under conditions in which the nitrite will do so readily. The reactions effecting the reduction of nitric oxide are discussed and it is suggested that hydrogen atoms from the decomposition of formaldehyde are responsible.

THE combustion process of aliphatic nitric esters, including cordites, may be divided into two broad phases. In the first, decomposition of the ester takes place very rapidly but the reactions do not proceed to chemical equilibrium since most of the nitrogen content of the system remains as nitric oxide. After a time delay, the length of which depends on the pressure, reduction of the nitric oxide in the reaction products appears to take place in a second flame zone in which thermodynamic equilibrium is reached. Up to quite high combustion pressures (e.g. 1 500 lb/in^2) this second phase of reaction is too remote from the burning surface of the ester to influence its rate of consumption and the latter is controlled almost entirely by the reaction in the first phase. For example at atmospheric pressure the secondary flame, involving final reduction of nitric oxide, is absent altogether yet stable flames of decomposing nitric esters (of sufficient energy) can still be obtained. In the case of ethyl nitrate[1] it has been shown by analyses of first-stage products that the greater part of the nitrogen content remains as nitric oxide and in the cooler flames of the propyl nitrates[2] products of the first stage of reaction include major quantities of nitrites and nitro compounds in addition to nitric oxide. An important observation from these flames was that although the greater part of the nitric oxide remained unreduced at the end of the atmospheric pressure reaction, a limited amount was reduced to nitrogen in every case and this reaction proceeded far more rapidly in the flame front than in the hotter and apparently equally reducing atmosphere of the products behind the flame front.

*Part of this work and papers concerned with the same subject by P. GRAY and M. W. T. PRATT and by A. R. HALL and H. G. WOLFHARD were presented and discussed together at the Sixth Symposium on Combustion, Yale University, 1956.

The low pressure, relatively low temperature reactions of nitric oxide are of prime importance in the combustion of nitric ester propellants: reduction of nitric oxide by organic molecules or hydrogen is usually a highly exothermic process, and the extent of such reactions occurring in the first, rate-controlling stage will be a major influence on the rate of burning.

Methyl nitrite will sustain a self-decomposition flame[3] at relatively low pressure (atmospheric) and the maximum temperature of this flame is too low for the rapid thermal decomposition of nitric oxide. The energy released in the flame must, nevertheless, depend entirely on oxidation of organic fragments by nitric oxide; certain unknown species are capable of reduction of nitric oxide with relative ease in this flame. Therefore, in addition to being of considerable interest itself, the methyl nitrite flame provides a very valuable system for the study of the low pressure, low temperature, flame reactions of nitric oxide which are important in nitric ester propellant combustion. The simplicity of the reactant is of particular advantage in the study of the reactions taking place in complex combustion processes.

A fairly detailed analysis of the changes of temperature and of reaction products and intermediates has been made in the pure methyl nitrite decomposition flame.

EXPERIMENTAL

Preparation and storage of methyl nitrite

Methyl nitrite is a gas at room temperature, condensing at −18°C to a yellow liquid. It was prepared from methanol, sodium nitrite and dilute sulphuric acid by the method of J. A. GRAY and D. W. G. STYLE[4]. The gas was condensed at −80°C and then redistilled *in vacuo*, the first and last fractions being rejected. The middle fraction was condensed into a two-litre metal cyclinder and stored at room temperature. As a precaution, the cylinder was fitted with a large disc designed to burst at 10 atm and was kept in a separate compartment away from the operator. Methyl nitrite has recently been shown[5] to be capable of detonation.

The infra-red (i.r.) spectrum of this bulk material did not differ from that of a purified sample so further purification of the nitrite was not considered necessary.

Burner and gas-sampling system

The methyl nitrite flame was stabilized very easily at atmospheric pressure in a flat flame burner[6] 3·8 cm in diameter. A diagram of the burner and sampling system is shown in *Figure 1*. In general features, the gas-sampling apparatus is similar to that used in studying the flame decomposition of ethyl and propyl nitrates[1, 2] and only the main differences are dealt with below. The Pyrex burner tube was surrounded by an outer glass tube, about 6 cm in diameter, carrying nitrogen. The flame was almost invisible and was detected using a shadow technique. The parallel incident light passing through the region of temperature gradient was focused to a bright

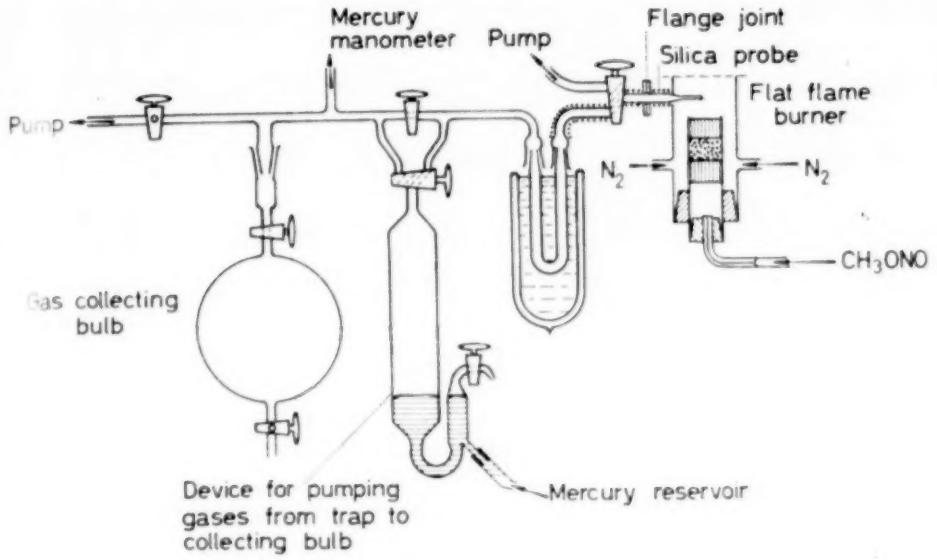

Figure 1. Burner and sampling apparatus

horizontal line (*Figure 2* shows a shadow photograph of the flame), and the sharply defined upper edge of this line was taken as an arbitrary zero level for all measurements through the flame; this zero corresponds to the position of the maximum temperature gradient in the flame front. Chemical compositions and temperature were measured from about 2 mm below to about 19 mm above this line.

A sample of the burning gas was withdrawn slowly (about 300 cm^3 in 5 to 10 min) from the flame by means of a silica probe (about 0·3 mm i.d., and 0·5 mm o.d.) attached to the all-glass apparatus by a small flange joint. The 3-way tap permitted air trapped in the dead-space of the probe to be drawn off via the other limb before sampling. The section of the

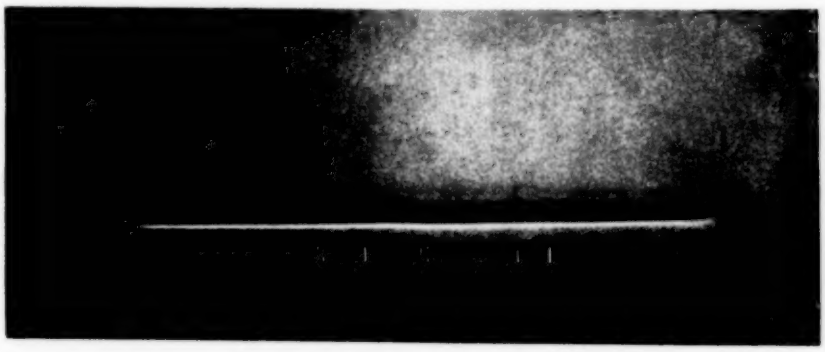

Figure 2. Shadowgraph of flame

system before the liquid nitrogen trap was heated electrically to about 100°C to prevent premature condensation of liquids.

Diluents could be metered and added to the methyl nitrite input through auxiliary lines. For the introduction of methanol and formaldehyde vapours, these lines and their flowmeters were heated electrically and the

supply of the vapour was fed from a vapour storage vessel in which liquid methanol or solid paraformaldehyde could be heated to give an adequate reservoir of pressure of the vapour.

Identification and analysis of products of combustion

The products were identified by their i.r. spectra. The sample was separated into a gas fraction (containing all substances volatile at −80°C), a vapour fraction (compounds volatile at room temperature), and a residual liquid fraction. The gas fraction was found to contain methyl nitrite, nitric oxide, carbon monoxide, methane, carbon dioxide, nitrous oxide and acetylene (also nitrogen and hydrogen, from chemical analysis), and the vapours consisted of methanol, water, hydrocyanic acid and ammonia. The spectrum of the vaporized liquid was examined using a heated i.r. cell and methanol, formaldehyde, hydrocyanic acid, water, formaldoxime and ammonia were identified. A non-volatile solid residue, having a fishy amine-like odour, remained after evaporation. The spectrum of the latter in methyl cyanide solution showed sharp absorption maxima at wavelengths of 5·95, 8·09, 9·90, 12·22 and 14·94 microns; this was almost identical to that of hexamethylenetetramine (prepared by the action of excess ammonia on formaldehyde in aqueous solution at room temperature) in the same solvent, for which maxima at 8·09, 9·91, 12·23 and 14·94 microns were obtained. Hexamethylenetetramine prepared by action of excess formaldehyde on ammonia in solution was not obtained in crystalline form but as a sticky solid, very similar to that resulting from methyl nitrite combustion. It showed similar absorption to pure hexamethylenetetramine but had an additional peak at 5·98 microns, presumably due to presence of formaldehyde. It was concluded that the solid left after evaporation of the liquid sample was hexamethylenetetramine mixed with formaldehyde. Since hexamethylenetetramine is not stable above about 300°C it was assumed that this material had formed in the cooling gas sample or in the trap. It is known to be formed rapidly in aqueous solution or in the vapour phase according to the overall equation

$$6H_2CO + 4NH_3 \rightarrow \underset{\text{(hexamethylenetetramine)}}{C_6H_{12}N_4} + 6H_2O \qquad \ldots\ldots[1]$$

Ammonia and formaldehyde are present in the flame gases, so the hexamethylenetetramine is quoted in *Figure 4* as NH_3 and H_2CO. The amount of water found in the trap was corrected according to equation 1 but the corrections were not large since the maximum amount of hexamethylenetetramine found was 1·9 mol per 100 mols methyl nitrite.

Complete quantitative analyses of the samples collected were carried out. The gas fraction was analysed chemically and by i.r. methods. The vapour fraction was estimated by i.r. measurements alone. Analysis of the liquid was accomplished by i.r. examination of the vaporized liquid in a cell maintained at 120°C. Silicone high-vacuum grease, to which titanium dioxide powder had been added in order to obtain a stiffer consistency, was used to make the airtight seals for this cell. About 10 mg of liquid was

weighed accurately into a small removable side arm to the cell, which was then refitted to the cell, cooled in liquid nitrogen, and pumped free of air. The cell was then placed in an electrically heated box fitted with sodium chloride windows, and the spectrum of the vaporized liquid recorded at 120°C. Calibration curves for the various components of the liquid were obtained by weighing the pure substance into the cell and vaporizing. It was found that water could not be analysed satisfactorily in the vapour phase by the i.r. method but it could be estimated directly by the Fischer titration method, since none of the other substances present in the liquid was found to interfere with the reaction.

Flame temperature measurements

Measurements of flame temperature were made with glass-coated platinum/platinum–10 per cent rhodium thermocouples, the overall thickness of which was not greater than 0·3 mm. The wires were stretched between silica rods mounted on a simple device designed to apply a small tension to them, thereby preventing sagging of the couple as a result of thermal expansion. The whole thermocouple system was mounted so that the couple was held horizontal in the flame and could be moved in a vertical direction by a screw device. The voltage from the thermocouple was quite steady even in the region of greatest temperature gradient. The inflection in the temperature distribution curve (*Figure 4*, at 1 mm) is thought to be real since there is supporting evidence from shadow photographs of the flame (*Figure 2*) which reveal a second shadow above the first. Smooth curves are obtained on each individual determination of the temperature distribution but the actual values of the maximum temperature showed some variation (see *Figure 4*); no correction was made for small radiation losses nor for any catalysis that may still have occurred on the glass coatings.

Flame propagation tests

The ability of certain gas mixtures, containing methyl nitrite, nitric oxide, formaldehyde, methanol, etc., to propagate flame was tested in a vertical glass cylinder about 5 cm i.d. and 25 cm long. A hot wire igniting coil was located towards the lower end of the tube and the latter was closed at the bottom by a wide pressure-release valve set to operate at 1 atm (abs.). The whole tube and the evacuating, filling and sampling leads were electrically heated to permit the testing of less volatile fuels. A diagram of the apparatus is shown in *Figure 3*.

Burning velocity

The burning velocity of pure methyl nitrite vapour was determined in the flat flame burner by dividing the volumetric rate of flow of the vapour leaving the burner port by the area of the disc of flame. The rate of flow at the burner port is higher than that at the entrance to the burner according to the degree of preheating taking place in the burner matrix. The burning velocity of the methyl nitrite flame relative to the vapour at 200°C, the steady degree of preheat in burner used, was found to be 7·3 cm/s.

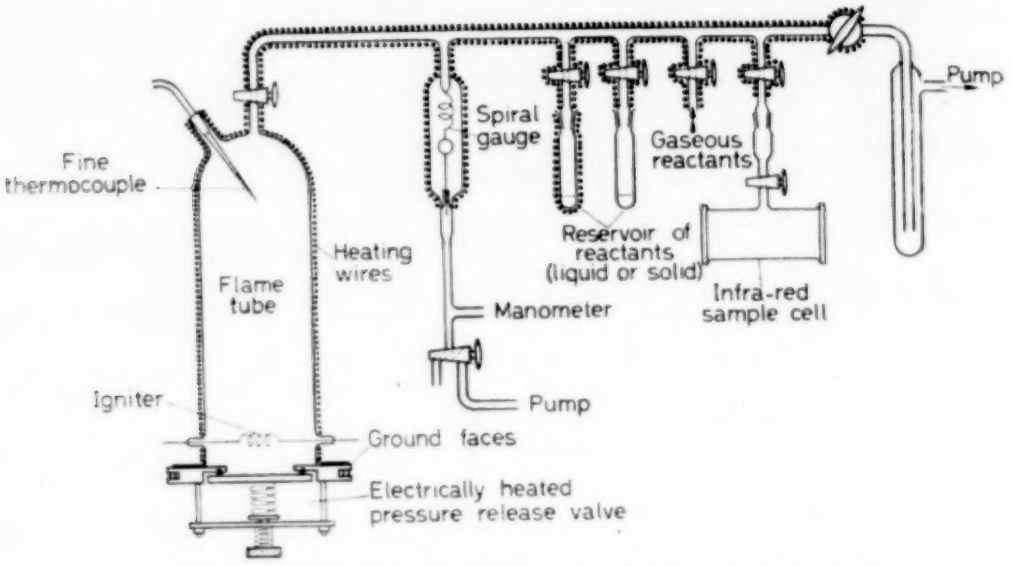

Figure 3. Arrangement of apparatus for flame propagation tests

RESULTS

The course of events taking place in the flame, as far as it is revealed by the changes in chemical composition of its (more stable) ingredients and in its temperature, is shown in *Figure 4*; the temperature distribution is given in the upper part of the graph and the quantitative combustion product distribution on the same distance scale below. It is considered that the analyses of the stable products are reasonably complete and give a reliable indication of the composition of the flame gases, i.e. changes taking place in the probe and trap are not extensive. The number of mols of the nitrite required to give the amounts of products shown in *Figure 4* is estimated from the mean of a carbon and a nitrogen balance, both of which seem fairly reliable. The balances are quite good considering the complexity of the mixture and the somewhat limited accuracy expected of certain i.r. analyses.

DISCUSSION

The main events in the flame may be briefly summarized as follows: the methyl nitrite vapour issuing from the burner port is heated to about 200°C by radiation from the flame on to the burner matrix and hence by conduction to the vapour. The nitrite then enters the flame zone and decomposition appears to be complete before the inflection in the temperature curve, i.e. below 700°C. The reaction in this first stage is almost quantitatively according to the overall reaction 2 which is approximately thermoneutral. (The thermochemical data used are mostly those given by Gray[3].)

$$CH_3ONO \rightarrow \tfrac{1}{2}CH_3OH + \tfrac{1}{2}CH_2O + NO - 1\ \text{kcal} \qquad \ldots [2]$$

Exothermic reaction then proceeds between the nitric oxide and the other products of reaction 2 or their degradation products, to give water and nitrogen. This reaction does not continue after the degradation of the methanol and the formaldehyde to carbon monoxide and hydrogen, which is complete about 9 mm from the flame front, and approximately one half

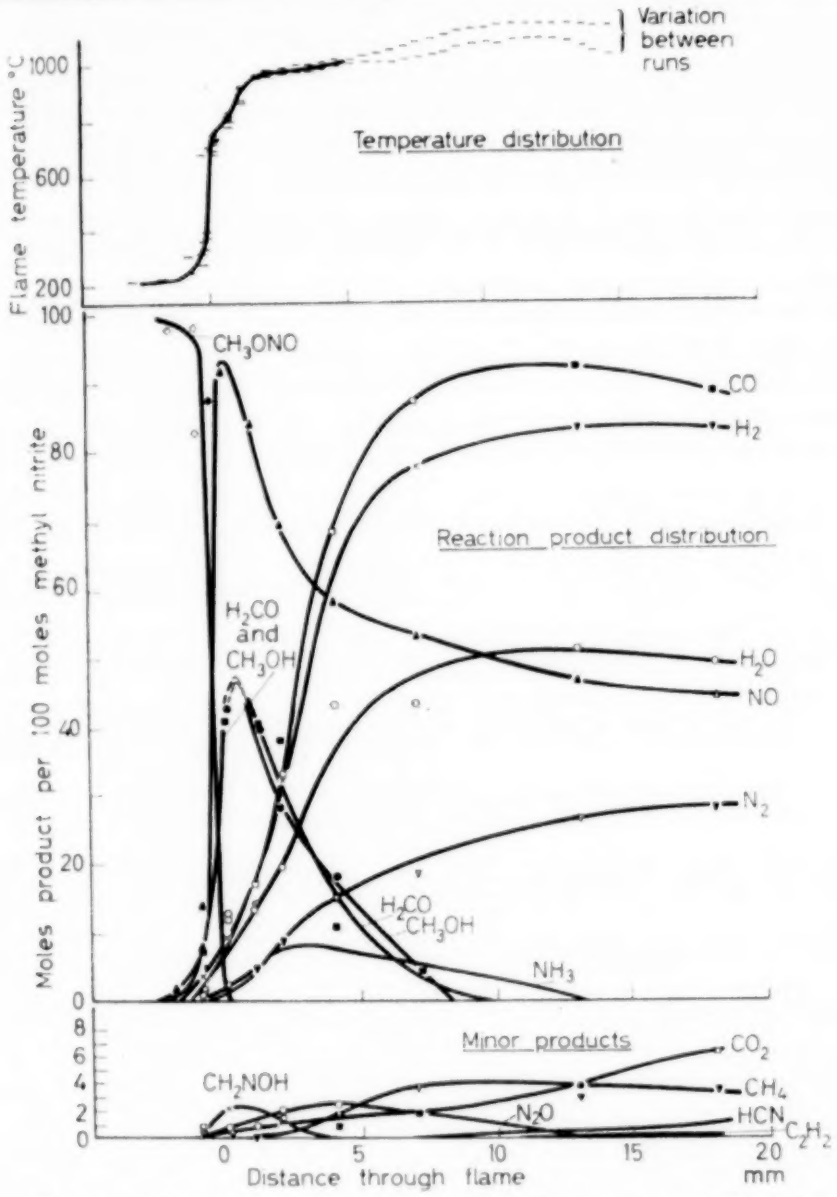

Figure 4. Temperature and product distribution in methyl nitrite flame

of the nitric oxide remains unreduced in the final gases at about 1 100°C. The reactions consuming the nitrous ester could be:

$$CH_3ONO \rightarrow CH_3O\cdot + NO - \sim 38\ \text{kcal} \quad \ldots\ldots [3]$$

$$CH_3O\cdot + CH_3ONO \rightarrow CH_3OH + CH_2O + NO + \sim 37\ \text{kcal} \quad \ldots\ldots [4]$$

Reaction 3 is considered to be the initial step in the thermal decomposition of methyl nitrite[7, 8] but the subsequent steps in the reactions of the products of 3 are still uncertain. E. W. R. STEACIE and G. T. SHAW[7] have suggested reactions 5 and 6 below to account for the main products:

$$CH_3O\cdot \rightarrow CH_2O + H\cdot - 25\ \text{kcal} \quad \ldots\ldots [5]$$

$$H\cdot + CH_3O\cdot \rightarrow CH_3OH + \sim 100\ \text{kcal} \quad \ldots\ldots [6]$$

Reaction 6 would seem unlikely as a major reaction in flames. F. O. RICE and E. L. RODOWSKAS[9], for ethyl nitrite, suggest another non-chain radical process in which the nitrous ester itself is attacked by radicals. The analogous sequence of reactions for methyl nitrite would be 3, 4 and 5 (above) and in addition the reaction 7 (below)

$$H\cdot + CH_3ONO \rightarrow H_2 + CH_2O + NO + 41\ \text{kcal} \quad \ldots . [7]$$

In this work there is evidence that reaction 7 does not take place to any appreciable extent since the amount of hydrogen found when all the nitrite has disappeared is quite small and this small amount is in any case probably formed from the decomposition of formaldehyde and methanol (see *Figure 4*). Although reaction 4 would seem the most feasible step to follow reaction 3, it has been assumed by Gray and Style[4] to be unimportant in the photodecomposition of methyl nitrite, and the analogous reaction in the ethyl nitrite decomposition (reaction 8) has been discounted by J. B. LEVY[10].

$$CH_3CH_2O\cdot + CH_3CH_2ONO \rightarrow CH_3CH_2OH + [CH_3\dot{C}HONO] \ldots . [8]$$

The presence of major quantities of nitrous oxide was reported in the work of Gray and Style and of Levy, and to explain this reactions 3 and 4 alone were, of course, inadequate. Gray and Style suggested that hydrogen atoms were produced in reaction 5 and some combined with nitric oxide to give HNO. The HNO produced nitrous oxide according to

$$2\dot{H}NO \rightarrow N_2O + H_2O + \sim 8\ \text{kcal} \quad \ldots . [9]$$

A similar source of nitrous oxide was suggested by Levy who considered NOH to be the result of reaction between ethoxy radicals and nitric oxide

$$CH_3CH_2O\cdot + NO \rightarrow NOH + CH_3CHO \quad \ldots . [10]$$

The NOH degenerated to nitrous oxide and water and perhaps also to nitric oxide, nitrogen and water. To account for the final products of the first stage of the flame decomposition (almost quantitatively to methanol, formaldehyde and nitric oxide), reactions similar to 9 and 10 are not necessary but it is possible that nitrous oxide is an intermediate in the formation of nitrogen in the *later* stages of the flame. Further evidence is required to decide whether reaction 4 alone follows 3 to give the first-stage products. A more complex route, starting with reaction 5 may take place at the higher temperatures in the flame front. Useful information on this matter is provided by the effects observed when nitric oxide is added to the flame: this is discussed later.

The nitric oxide formed in the flame front is reduced in what will be termed here the second stage of the flame, that is, the phase of reaction which takes place in the products of the initial decomposition (beyond 0·5 mm, *Figure 4*). The only reactants in major quantities at the beginning of the second stage are, as already stated, nitric oxide, methanol and formaldehyde which make up 42, 19 and 20 per cent by volume, respectively, of the gases. The exothermic reactions which maintain flame propagation in methyl nitrite must take place in these ingredients and it is important to note that reduction of nitric oxide virtually ceases when all the methanol

and the formaldehyde has decomposed to carbon monoxide and hydrogen. The methanol and formaldehyde decompose in the flame at identical rates over the temperature range ~750 to 1 000°C in spite of different individual stabilities. It seems likely that the two decompositions are linked together, perhaps by a common intermediate such as a hydrogen atom (cf. radical-sensitized decompositions in mixtures of acetaldehyde and formaldehyde[11]). Hydrogen atoms have been shown[12] to be present in the pyrolysis of formaldehyde and a separate study[13] of this pyrolysis at ~600°C in the presence of nitric oxide has shown that small quantities of the latter strongly inhibit the reaction (until the nitric oxide is consumed) and larger amounts increase the rate of decomposition. The nitric oxide is converted to nitrous oxide, nitrogen, ammonia, hydrocyanic acid and cyanic acid, and water is the main oxidation product, only small quantities of carbon dioxide being found.

It would be reasonable to suggest that hydrogen atoms, produced in the decomposition of formaldehyde, might be responsible for the reduction of nitric oxide in both the methyl nitrite flame and the formaldehyde pyrolysis.

In the second stage of the flame the nitric oxide could become involved in the decomposition of the formaldehyde and methanol in the following way:

$$R\cdot + H_2CO \rightarrow RH + H\dot{C}O \quad \ldots.[11]$$

$$H\dot{C}O \rightarrow H\cdot + CO \quad \ldots.[12]$$

$$H\cdot + H_2CO \rightarrow H_2 + H\dot{C}O, \text{ etc.} \quad \ldots.[13]$$

$$H\cdot + CH_3OH \rightarrow H_2 + \dot{C}H_2OH, \text{ etc.} \quad \ldots.[14]$$

$$H\cdot + NO \rightarrow HNO \quad \ldots.[15]$$

$$HNO + NO \rightarrow \begin{matrix} N_2O + \cdot OH \\ \downarrow \\ N_2 \end{matrix} \quad \ldots.[16]$$

$$\cdot OH + RH \rightarrow H_2O + R\cdot \quad \ldots.[17]$$

Such a sequence could account for the sustained decomposition of the aldehyde and alcohol with partial reduction of the nitric oxide to give water as oxidation product. C. N. HINSHELWOOD *et al.*[14, 15] concluded that hydrogen atoms do not take part in the thermal reaction between nitric oxide and hydrogen at 1 000°K where J. A. TAYLOR and C. TANFORD[16] suggest that they are responsible for the reduction of nitric oxide according to reaction 15 above, which is followed by:

$$2\ HNO \rightarrow N_2O + H_2O \quad \ldots.[9]$$

$$N_2O + H\cdot \rightarrow N_2 + \cdot OH + 62 \text{ kcal} \quad \ldots.[18]$$

$$H\cdot + HNO \rightarrow H_2 + NO + \sim 55 \text{ kcal} \quad \ldots.[19]$$

G. K. ADAMS, W. G. PARKER and H. G. WOLFHARD[17] do not favour reactions such as 15 and 9 as steps in the high temperature flame of nitric

oxide and hydrogen but a scheme suggested by A. I. ROZLOVSKII[18] includes such steps as:

$$H\cdot + NO \rightarrow NOH \quad \ldots.[20]$$

$$\dot{N}OH + NO \rightarrow N_2 + H\dot{O}_2 \quad \ldots.[21]$$

There is good evidence[19] that nitric oxide reacts readily with hydrogen atoms, at least at low temperatures, to give HNO. J. A. GRAY (reported by P. GRAY[20]) has suggested that the formation of major quantities of nitrous oxide and nitrogen in the photolysis of methyl nitrite, rather than nitric oxide as in thermal decomposition, is due to the reduction of nitric oxide by hydrogen atoms, the latter being formed from $CH_3O\cdot$ in the early stages of decomposition by the excess energy of the irradiating light or, in later stages, by the photolysis of formaldehyde.

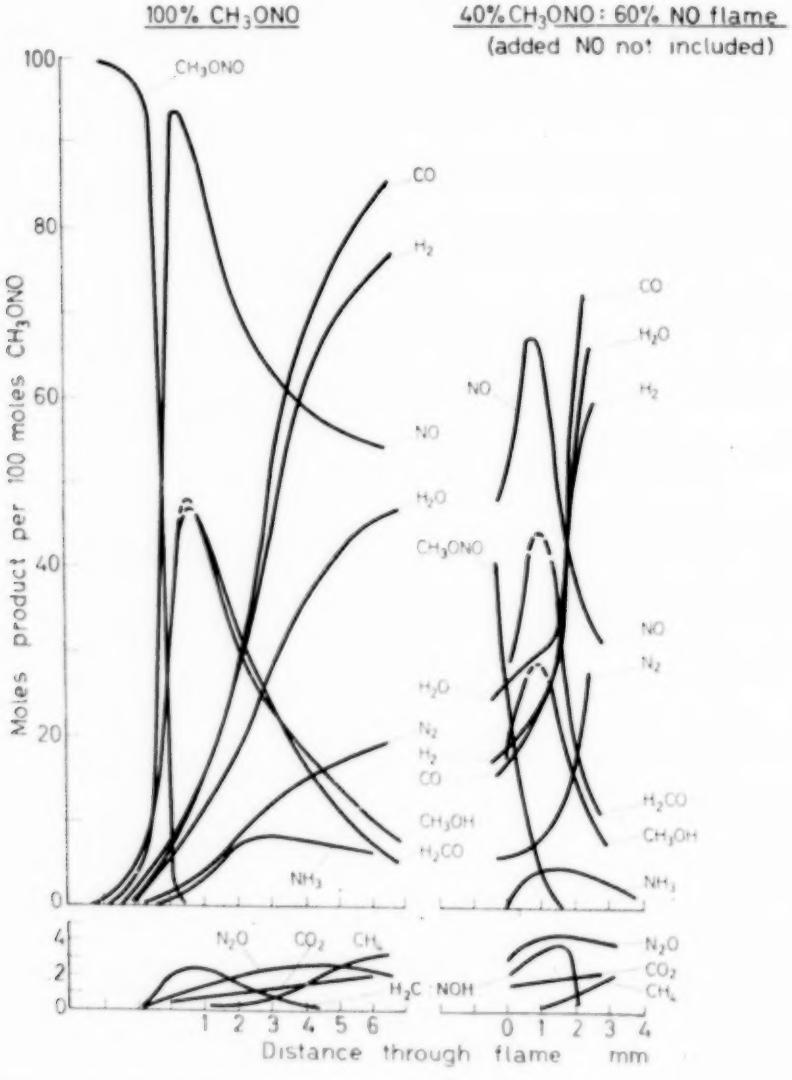

Figure 5. Comparison of concentration profile in the methyl nitrite flame and a 40 CH_3ONO 60 NO *flame*

Some auxiliary experiments were performed to provide a little more evidence on the above considerations.

Effect of additions of nitric oxide, nitrous oxide, formaldehyde and methanol to the flame

(a) *Addition of nitric oxide*—In the explosion of methyl nitrite vapour in the glass cylinder at a constant pressure of 1 atm, it was found that the addition of nitric oxide to the nitrite increased the vigour of the explosion. This seems a rather remarkable fact when it is remembered that about 50 per cent of the nitric oxide produced by the pure nitrite remains unchanged in the final flame gases. Also, the dilution limit of inflammability of methyl nitrite in nitric oxide is very much lower than that of methyl nitrite in nitrogen. All mixtures of more than 17·6 per cent (vol) of methyl nitrite in nitric oxide are, in fact, capable of propagating flame at atmospheric pressure whereas the dilution limit of methyl nitrite in nitrogen is 42·8 per cent. Dilution of methyl nitrite with four times its own volume of nitric oxide does not result in complete oxidation of the fuel. The flame is not the usual lower-limit flame in which the deficient fuel is oxidized completely as occurs when methyl nitrite is diluted with nitrous oxide or air. In these latter cases lower-limit values of ~5·1 per cent and ~3·6 per cent are obtained and oxidation is complete. In fact, certain methyl nitrite–nitric oxide mixtures can sustain the propagation of either a 'cool' flame, similar in characteristics to the methyl nitrite decomposition flame, or, if a high temperature ignition source is applied, a normal 'hot' nitric oxide–fuel flame accompanied by complete oxidation. If the cool flame is established in certain mixtures, the products can be ignited so that the ensuing hot flame flashes back and overtakes the cool flame.

A limited number of probe-sampling experiments were performed in a flame diluted with about 60 per cent by volume of nitric oxide. Product distribution in this (cool) flame is plotted, over a limited range, in *Figure 5* and compared with the pure methyl nitrite flame. In the figure the *added* nitric oxide is not included, only the nitric oxide derived from the methyl nitrite being shown.

It is seen that considerably more nitric oxide has been reduced to nitrogen in the nitric oxide-diluted system and water is the main overall oxidation product of the reaction. The amount of formaldehyde is little changed in contrast to the methanol which is much reduced. Such changes might well be the result of a reaction between nitric oxide and $CH_3O\cdot$ (reaction 22 below) competing to some extent with the methanol-producing reaction 8 when a high concentration of nitric oxide is present.

$$CH_3O\cdot + NO \rightarrow HNO + H_2CO + \sim 24\ \text{kcal} \qquad \ldots . [22]$$

Part of the highly exothermic reduction of nitric oxide to nitrogen is then advanced into the normally almost thermoneutral decomposition stage of the flame. Flame speed for the 60 per cent nitric oxide mixture is 9·7 cm/s.

(b) *Addition of nitrous oxide*—Nitrous oxide is found in the flame up to ~13 mm downstream. Its appearance and disappearance seem to be linked with those of nitric oxide and ammonia. The slope of the nitrous

oxide curve from 4 to 13 mm in *Figure 4* may represent either the rate of disappearance of nitrous oxide produced in the early stages of the flame or the stationary concentration of nitrous oxide which is an intermediate in the formation of nitrogen from nitric oxide, as reactions 15 and 16 would demand.

Additions of nitrous oxide to the flame did not appreciably increase its concentration in the products. *Table 1* shows some i.r. analyses of combustion products, including nitrous oxide, of methyl nitrite–nitrous oxide mixtures (flame propagation in tube). The nitrous oxide curve in *Figure 4* therefore probably represents the stationary concentrations at each point rather than a nitrous oxide decomposition curve.

It is seen, incidentally, that carbon monoxide is not oxidized by the additional nitrous oxide until large amounts of the latter have been added when the flame temperature might be expected to have increased sufficiently for initiation of the reactions of the water gas equilibrium which give rise to carbon dioxide indirectly. Water must be the main oxidation product.

Table 1. Percentage (by volume) of some products from methyl nitrite–nitrous oxide mixtures (i.r. analyses only)

Product	*Mixture composition* $CH_3ONO : N_2O$			
	100 : 0	95 : 5	92 : 8	81 : 19
N_2O	1·4	1·3	2·0	2·1
CO	28·0	27·0	27·0	27·0
CO_2	4·4	2·8	3·8	6·0
NO	19·4	17·5	18·8	10·9
CH_3OH	5·3	3·5	3·1	2·0
CH_3ONO	3·1	2·6	2·7	2·5
HCN	0·5	0·3	0·3	0·3

(c) *Addition of formaldehyde and methanol*—Since reduction of nitric oxide ceases when decomposition of formaldehyde and methanol is complete in the flame it was considered that additional amounts of these materials introduced into the flame would prolong the nitric oxide reduction and, if added separately, would give information regarding the effectiveness of each in this respect.

Tables 2 and *3* show that an increase in the methanol or formaldehyde content of the flame has little effect on the amount of nitric oxide reduced.

Slightly more nitric oxide is reduced by additional methanol, with corresponding increase in water. The reduced nitric oxide appears as nitrous oxide and ammonia rather than nitrogen in the cooler flame. The formaldehyde persists longer. The added methanol and formaldehyde are little more than coolants in the flame. These results are not compatible with the idea that the reduction of nitric oxide ceases because the formaldehyde and methanol have disappeared. It may be that the cooling effect of the extra fuel (in a fuel-rich system) overcomes its promoting effect or that it is the maintenance of the sensitizing reaction 11 that is important. Some static experiments on flame propagation in mixtures of nitric oxide, methanol and formaldehyde are of interest in this connection.

Table 2. Products of methyl nitrite–methanol flames

Distance from arbitrary zero, mm	7·3		13·3	
Mixture composition (by volume) $CH_3ONO:CH_3OH$	84 : 16	100 : 0	80 : 20	100 : 0
Product				
NO	49·6	52·6	40·2	46·3
CH_3OH	13·0	4·5	5·1	0
H_2CO	7·9	4·5	6·6	0
H_2	90·9	77·2	104	82·7
CO	93·2	86·7	108	91·8
CO_2	1·5	1·9	1·7	3·9
H_2O	55·4	(43·0)	54·4	50·6
N_2	18·8	18·4	23·2	26·4
N_2O	3·0	1·9	2·9	0
CH_4	3·7	3·9	3·4	3·0
NH_3	6·8	5·1	7·6	0·4
HCN	0	0·1	0	0·4
C_2H_2	0	0	0	0·4

Table 3. Products of methyl nitrite–formaldehyde flame
Distance from arbitrary zero: 13·3 mm

Product	*Mixture composition (by volume)* $CH_3ONO : H_2CO$	
	82 : 18	100 : 0
NO	48·3	46·3
CH_3OH	8·0	0
H_2CO	6·1	0
H_2	96·4	82·7
CO	97·9	91·8
CO_2	5·5	3·9
H_2O	~49	50·6
N_2	23·5	26·4
N_2O	1·1	0
CH_4	4·1	3·0
NH_3	2·3	0·4
HCN	0·2	0·4
C_2H_2	0·2	0·4

Flame propagation in some static mixtures

The following points summarize experiments on the propagation of flame in static nitric oxide–fuel mixtures preheated to about 100°C in the 5 cm i.d. vented tube.

Methyl nitrite readily ignites with a hot wire and propagates freely, whereas a mixture of 2 volumes of nitric oxide, 1 volume of formaldehyde and 1 volume of methanol, such as that produced by the thermoneutral decomposition of methyl nitrite, will not propagate flame. Methyl nitrite has to be added to the latter mixture before it can be ignited; the limiting

amount was not determined but it is more than 11 per cent and less than 38 per cent. Only about 17 per cent methyl nitrite has to be added to a 1 : 1 mixture of formaldehyde–nitric oxide to make 'cool' flame propagation possible whereas about 33 per cent is required for a 1: 1 methanol–nitric oxide mixture. Nitrogen dioxide will sensitize 1 : 1 formaldehyde–nitric oxide mixture at much smaller concentrations than methyl nitrite, as little as 2 per cent being effective. Small additions of bromine or methyl iodide (5 per cent) also sensitized this mixture but no sensitizer rendered the 1 : 1 methanol–nitric oxide mixture capable of propagating a flame. A mixture of equal volumes of hydrogen, carbon monoxide and nitric oxide (i.e. equivalent to 1: 1 formaldehyde–nitric oxide) could not be ignited, with or without the sensitizer, under the present experimental conditions. It is significant that the spontaneous ignition temperature of a $1\,H_2CO/1\,NO$ mixture (620°C at 430 mm of mercury) is much lower than those quoted[21] for hydrogen–nitric oxide (1 320°C at 1 atm) or carbon monoxide–nitric oxide (1 450°C at 1 atm) mixtures.

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A Review of Some Unusual Stationary Flame Reactions

W. G. PARKER

Air flames on account of their wide application have dominated combustion research hitherto. This brief review indicates that self-propagating flames are not confined to oxidation reactions by oxygen or even to oxidation reactions in the broadest sense.

COMBUSTION research, which may be said to have begun with Sir Humphrey Davy's experiments nearly 150 years ago, has grown enormously in recent times and now covers a very wide field. Davy was particularly concerned with flame as the combustion of an explosive mixture of an inflammable gas and air and few people even today regard it simply as a phenomenon which may accompany any vigorous chemical reaction in the gas phase. In the last decade, however, a number of studies have been reported on flames which might be termed unusual because they do not depend on air or oxygen. The reasons for these studies lie partly in pure scientific interest and partly in the need for a better knowledge of many reactions which occur in the combustion of propellants and explosives, or which constitute chemical processes or hazards in industry.

SELF-DECOMPOSITION FLAMES

To underline the fact that air is not essential for the production of a flame let us consider first a few simple compounds which in the gaseous state can decompose in a self-propagating reaction. Although it has long been known that acetylene could provide a self-decomposition flame, one of the first stationary self-decomposition flames to be studied in detail is that of hydrazine.

Hydrazine

The hydrazine flame was established like a bunsen flame on a circular burner at atmospheric pressure by R. C. MURRAY and A. R. HALL[1]. An aqueous solution of hydrazine was totally vaporized by passing it through a hot tube at 170°C and the vapour was fed to the bottom of a vertical burner tube about 45 cm long and a few millimetres in diameter, which was heated to about 150°C. The vapour was ignited in air at the tip of the burner and a diffusion flame was obtained which had an inner cone due to hydrazine decomposition. An outer glass tube was then placed round the burner which acted as a Smithells separator and eliminated the air diffusion flame. The inner cone then remained as a stationary decomposition flame of hydrazine and measurements were made of the burning velocity, temperature and products of decomposition.

Flames were obtained with hydrazine concentrations between 60·9 and 97·3 per cent by weight, and were a pale brownish yellow due partly to sodium impurity and partly to emission of the ammonia α-bands (attributed to NH_2). The luminosity increased with the hydrazine concentration. The flame speeds which were calculated from the area of the luminous reaction

zone increased with hydrazine concentration from 30 to 190 cm/s and by extrapolation the flame speed of pure hydrazine vapour was estimated to be about 200 cm/s. Products from the decomposition flame of 97 per cent hydrazine were collected and analysed and found to conform fairly closely with the reaction

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2 \quad \ldots\ldots [1]$$

This result is interesting because it is associated with a theoretical flame temperature of about 1 900° K which is more than 500° higher than the temperature which would be achieved if the reaction was

$$N_2H_4 \longrightarrow N_2 + 2H_2 \quad \ldots\ldots [2]$$

The measured flame temperature was somewhere between the two theoretical values but the method used was not very accurate and erred on the low side. The formation of ammonia in a flame at these temperatures is evidence that chemical equilibrium is not achieved in the reaction zone.

On the mechanism of the homogeneous decomposition of hydrazine there has been considerable speculation and several attempts have been made to predict the flame velocity. The assumption made, that the reaction is first order and that the fission of the N—N bond is the rate-controlling step in the flame, is probably wrong, however, although it appeared to be supported at first by the experimental results of G. K. ADAMS and G. W. STOCKS[2]. More recent measurements of flame speeds by P. GRAY and J. C. LEE[3] on gaseous hydrazine at low pressure in a closed bomb have shown that the speed is virtually independent of pressure indicating that the overall reaction is second order. Moreover, the activation energy deduced from the application of Semenov's theory for a second order reaction to the results of flame propagation in mixtures with inert diluents was 36 kcal/mole. This shows that the rupture of the N—N bond in the N_2H_4 molecule which requires an energy of 60 kcal/mole is not the rate-determining step. A chain reaction is probably involved and a detailed mechanism in which H atoms and NH_2 radicals are chain carriers has been put forward[2]. The constancy of the burning velocity with pressure was shown also by A. R. HALL and H. G. WOLFHARD[4] using a burner method at pressures of 3, 7 and 15 mm of mercury, the results agreeing very well with the original measurements at atmospheric pressure.

Hydrogen peroxide

Hydrogen peroxide liberates heat on decomposition into steam and oxygen

$$\underset{\text{(liq)}}{H_2O_2} \longrightarrow \underset{\text{(gas)}}{\tfrac{1}{2}O_2} + \underset{\text{(gas)}}{H_2O} + 12{\cdot}99\ \text{kcal} \quad \ldots\ldots [3]$$

The pure liquid or very concentrated aqueous solutions may be detonated if confined in heavy walled containers and strongly initiated but can be handled with safety in ordinary containers made from compatible materials such as aluminium or glass. Hydrogen peroxide vapour, however, is readily ignited by a flame, spark, hot wire or a catalytic surface, and will propagate a decomposition flame. It was shown by A. B. HART[5] that this flame could be stabilized on a jet or near the surface of the boiling liquid.

The minimum concentration of hydrogen peroxide vapour which will propagate a flame was investigated by C. N. SATTERFIELD, G. M. KAVANAGH and H. RESNICK[6] who found that the limiting value depends upon the pressure and the nature of the diluent gas. At 760 mm of mercury pressure, for example, the limit in water vapour is 26 mole per cent of hydrogen peroxide vapour while at 200 mm of mercury pressure the concentration must be increased to 32·5 mole per cent in the same diluent. The corresponding adiabatic flame temperatures were calculated to be 780°C and 880°C respectively and these temperatures are interesting because they show that this decomposition flame will propagate at a lower temperature level than the majority of air oxidation flames (except hydrogen) in which the limit mixtures have a flame temperature of about 1 200°C.

At ordinary temperature the vapour pressure of hydrogen peroxide is too low to produce a dangerous concentration of the vapour above the liquid in a container but at elevated temperatures such as those used in distillation and other operations the critical vapour concentration for flame propagation might be reached.

There is no published information on the velocity of the decomposition flame or its tendency to burn to detonation. The laminar flame speeds which depend on the vapour concentration or more correctly on the flame temperature are probably quite moderate (<100 cm/s). From Hart's work it is obvious that measurements could be made using the bunsen cone method with flames stabilized on a heated burner.

The mechanism of the homogeneous thermal decomposition which occurs in the flame is believed to be rupture of the O—O bond followed by reactions between the OH radicals and the H_2O_2 molecule

$$H_2O_2 = 2OH \quad \ldots . [4]$$

$$HO + H_2O_2 = H_2O + HO_2 \quad \ldots . [5]$$

$$HO_2 + H_2O_2 = H_2O + HO + O_2 \quad \ldots . [6]$$

The formation of a hydroxyl radical in reaction 6 indicates that a chain reaction could occur, and the possibility of a chain is clearly demonstrated by the photochemical decomposition of hydrogen peroxide where quantum yields up to 100 have been observed by G. KORNFELD[7]. It appears unlikely that branched chain reactions play a significant part in the flame decomposition, however[6].

Acetylene

The explosive nature of acetylene even in the absence of air or oxygen has been known for a long time and, because of the wide use of acetylene first as a source of lighting and later in oxyacetylene welding and as a starting point in chemical synthesis, several investigations have been made of the conditions under which ignition and explosion can occur[8]. The main interest hitherto has been from the safety point of view but as long ago as 1925 D. ALEXEJEW[9] is reported to have studied the effects of pressure, temperature and various additives on the ignition and propagation of flames in tubes. More recently W. E. PROUT and R. C. ANDERSON[10] have made

similar studies of flame propagation in an attempt to understand the mechanism of decomposition. The flame speeds measured in non-detonative combustion of acetylene at pressures between 1 and 2 atm are of the order of 10 to 20 cm/s and in theory a stationary self-decomposition flame could be established on a burner. In practice, however, the flame produces a large quantity of carbon which builds up on the burner mouth and chokes the flame, and it has been necessary to forgo the advantages of a stationary flame and to study the flame as it travels through the vapour in a tube. Heavy carbon formation and a relatively high critical pressure below which acetylene will not propagate a non-detonative flame are the two outstanding characteristics of the combustion.

The overall reaction associated with the flame propagation is

$$\underset{\text{(gas)}}{C_2H_2} \longrightarrow \underset{\text{(solid)}}{2C} + \underset{\text{(gas)}}{H_2} \qquad \Delta H_{293} = -54{\cdot}9\ \text{kcal/mole} \qquad \ldots [7]$$

and unless the carbon appears in the solid phase the reaction is not exothermic. Hydrogen and solid carbon are in fact the major products after combustion but the steps by which these are reached are evidently very complex[11].

The spectrum of the decomposition flame is not informative. It was found by W. W. Robertson, N. B. Humphrey and R. C. Anderson[12] to consist of a continuum only with no evidence of any bands such as C_2 or CH. C_2 bands were obtained by A. R. Fairbairn and A. G. Gaydon[13] at the higher temperatures prevailing for decomposition in a shock tube, but G. Porter[14] has evidence from flash photolysis experiments that C_2 molecules are not essential intermediates in the formation of carbon from acetylene.

FLAMES SUPPORTED BY VARIOUS OXIDIZERS

Nitric esters, nitric acid and the oxides of nitrogen

A group of compounds which readily produce self-decomposition flames are the nitric esters but before discussing the recent work on these it will be convenient to describe some flames supported by the oxides of nitrogen.

Nitrous oxide flames—Nitrous oxide (N_2O) is well known for its similarity to oxygen as a supporter of combustion and for its use in anaesthetics. The latter application has given rise to a number of investigations of the limits of inflammability in nitrous oxide of a wide variety of organic vapours such as ethers and alcohols.

H. B. Dixon and W. F. Higgins[15] substituted nitrous oxide for air in small jets of premixed gases and observed the change in size and character of the flames. They noted that the hydrogen flame was enlarged and had a luminious inner cone surrounded by an apricot coloured zone which appeared to give a continuous spectrum while outside this was a third zone of greenish grey colour. Flames of methane and ethylene were smaller and more brilliant white than the corresponding air flames. The structure and spectrum of these flames have been more fully examined since by A. G. Gaydon and H. G. Wolfhard[16] and by H. G. Wolfhard and

W. G. PARKER[17]. The inner cone of the premixed hydrogen–nitrous oxide flame has a yellow cap which varies in intensity with the mixture ratio. OH bands are strongly emitted from the inner cone and bands of NH, NH_2 and NO(γ) are also emitted. The outer cone emits only OH bands. At low pressure when the reaction zone is somewhat extended the NH bands are found to have their maximum intensity at the base of the flame while the NH_2 bands occur a little later. The emission of these bands which are not present in premixed flames of hydrogen–oxygen and nitrogen suggests that nitrous oxide reacts directly with hydrogen and supports the observations of Dixon and Higgins who found no evidence of the decomposition of nitrous oxide before its reaction with hydrogen at temperatures up to 600°C. In diffusion flames with hydrogen, however, nitrous oxide apparently undergoes thermal decomposition in the preheating zone of the flame because all the banded spectra are missing with the exception of OH.

With hydrocarbons the inner cone of the premixed flame is bluish purple for stoichiometric mixtures and emits C_2, CH, NH, CN, OH and NO bands and again only OH in the burnt gases. As the proportion of fuel is increased the inner cone develops a halo from which C_2 and CN bands are emitted. In fuel-rich mixtures carbon formation also occurs and originates at the base of the flame. Lean flames show a green radiation in the interconal gas which is attributed to the association reaction NO + O. The nature of the spectra from the hydrocarbon flames again suggests that the mechanism of the reactions is complex.

The flame velocities of mixtures of nitrous oxide with hydrocarbons and nitrogen were determined by E. BARTHOLOMÉ[18] and are about half the velocities of the corresponding mixtures of oxygen with hydrocarbons and nitrogen which have the same flame temperature. Stoichiometric mixtures of hydrogen and nitrous oxide have a burning velocity of about 400 cm/s which is greater than that of the corresponding air flame (*ca.* 260 cm/s) but rather less than half the speed of the oxygen flame (*ca.* 900 cm/s). These velocities appear to be nearly independent of pressure.

C. J. S. M. SIMPSON and J. W. LINNETT[19] measured the burning velocities of mixtures of nitrous oxide and carbon monoxide and found that the effect of composition with water vapour and nitrogen as diluents was largely what might be predicted from the results of the low temperature kinetics but not entirely so.

Nitric oxide flames—Flames supported by nitric oxide (NO) and by nitrogen dioxide (NO_2) have some very interesting characteristics largely due to the unusual nature of nitric oxide. Although this compound is strongly endothermic it possesses a remarkable thermal stability and it is necessary to preheat the gas to 1 300°K before a stationary self-decomposition flame can be obtained. The flame which has a large quenching diameter and requires a high-temperature source for ignition has a temperature of about 3 000°K and propagates at a low velocity of a few cm/s. This velocity agrees with theoretical values calculated on the assumption that the reaction is bimolecular[20]. Such a mechanism is compatible with the spectrum of the flame which contains only the Schumann–Runge oxygen bands together

with OH bands due to the presence of traces of water. NH bands are not observed.

Contrary to general belief any fuel will burn with nitric oxide given the correct conditions which take into account the large quenching diameters and high ignition energies which may be required. Flames with hydrogen, ammonia and hydrocarbons have been studied by G. K. ADAMS, W. G. PARKER and H. G. WOLFHARD[21] and two clearly distinguishable reaction mechanisms have been established.

In the hydrogen–nitric oxide flame the temperature is about 3 100°K which is 100° above the temperature of the self-decomposition flame mentioned above. It is not therefore necessary to preheat the gases but an igniting source of comparable temperature is required and a burner of at least 2 cm diameter at 1 atm pressure. The hydrogen flame is visually similar to the decomposition flame. OH and O_2 bands are again the principal emitters and NH bands are absent. In absorption the NO (γ bands) show that the nitric oxide decomposes in the reaction zone whatever the mixture strength and only small concentrations corresponding to equilibrium amounts appear in the burnt gases. It has also been found that the introduction of nitric oxide into a hydrogen diffusion flame in air does not bring about reaction between nitric oxide and hydrogen because the temperature is not sufficiently high to start the nitric oxide decomposition reaction. These and other experimental facts led Adams and his co-authors to the conclusion that hydrogen reacts with oxygen after the nitric oxide has undergone self-decomposition. This conclusion is rejected by A. I. ROZLOVSKII[20] who considers that the mechanism is termolecular.

In contrast to hydrogen, ammonia burns readily with nitric oxide. Although the stoichiometric flame temperature is about 170° lower than that of the hydrogen flame, ammonia is readily ignited on a burner of about one tenth the diameter and the flame is about twice as fast. The most important observation, however, is that in mixtures rich in nitric oxide, oxygen cannot be detected and the NO (γ) bands are strong in absorption. The explanation of these differences probably lies in the ability of nitric oxide, by virtue of its unpaired electron structure, to react with free radicals such as NH_2 and NH which are formed in the degradation of ammonia. Although the activation energy required for the thermal decomposition of ammonia is actually higher than that of nitric oxide, degradation of ammonia can probably be brought about by a more favourable chain process involving hydrogen atoms and hydroxyl radicals present in the flame.

The combustion of hydrocarbons with nitric oxide has some of the characteristics of both the hydrogen and the ammonia flame. The flames have a well defined inner cone which is violet coloured and resembles that of nitrous oxide–hydrocarbon flames with emission of C_2, CH, NH and CN bands, the last two being detectable also in absorption. In fuel-rich mixtures the inner cone develops a red mantle, while in nitric oxide-rich flames a diffuse second cone is observed on top of the first and above this region oxygen is detectable in absorption. The interpretation of these results aided by other observations is that the nitric oxide does not decompose thermally and produce oxygen in the inner cone but undergoes direct

reaction with radicals formed by the fuel. This is supported by the fact that excess excitation which is a characteristic of the inner cone of hydrocarbon–oxygen flames was not detected in the inner cone of the ethane–nitric oxide flame.

Some excess excitation was observed in the acetylene flame, however, which can be explained on the supposition that nitric oxide is partially decomposed at the higher temperature of this flame.

Nitrogen dioxide flames—Some of the properties of nitric oxide flames influence the character of flames supported by nitrogen dioxide. The hydrogen–nitrogen dioxide flame for example does not burn to completion and the flame temperature for the stoichiometric mixture is found to be only 1 550°C compared with an estimated temperature of 2 660°C. The gases burn very readily on small burners of 1 mm diameter and the burning velocity is comparatively high but the nitrogen dioxide decomposes into nitric oxide and oxygen and it is only the latter which reacts with the hydrogen. There is only one reaction zone and this emits a yellow continuum. Strong nitric oxide absorption bands are present in the burnt gases which supports the belief that nitric oxide does not play a major part in the reaction because the temperature is below the self-decomposition temperature of nitric oxide.

In hydrocarbon flames with nitrogen dioxide there are two visible reaction zones which are separated by distances up to 2 mm depending on the composition of the gases. The first zone is yellow and not very intense at 1 atm pressure; the spectrum is continuous from the red into the blue giving the overall impression of yellow. The second zone is blue and the emission spectrum is similar to that of nitric oxide burning with the same fuel. Thus the indications are that the combustion takes place in two steps, the first consisting of the decomposition of nitrogen dioxide and a hydrocarbon–oxygen reaction diluted with nitric oxide, and the second which is the hotter zone consisting of reaction between partly oxidized fuel and nitric oxide diluted by the products of the first zone. Recent studies of *n*-butane–nitrogen dioxide flames are broadly in agreement with this[22, 23].

Nitric acid flames—A study has also been made recently by M. H. BOYER and P. E. FRIEBERTSHAUSER[24] of hydrocarbon flames supported by nitric acid vapour. A close structural resemblance was found to the nitrogen dioxide flames, and nearly the stoichiometric quantity of nitric oxide was found in the analyses of the non-condensable products of combustion. This nitric oxide would not react without the aid of secondary air in a diffusion flame. These results are not surprising if the acid first breaks down by the step which is known to occur in thermal decomposition at rather lower temperatures, viz.

$$HONO_2 \longrightarrow HO + NO_2 \qquad \ldots . [8]$$

Nitric ester flames—Let us now return to the nitric esters, the simpler members of which have been burned as stationary decomposition flames. Methyl nitrate vapour was readily ignited on a 20 mm diameter burner at a reduced pressure of about 13 mm of mercury by P. GRAY, A. R. HALL and H. G. WOLFHARD[25], and under these conditions the reaction zone was in

the form of a blue disc about 1 mm thick followed by a thin dark space and then by a luminous conical region of orange red radiation. Spectroscopic examination showed clearly that formaldehyde bands were emitted in the blue zone but that the orange red region was in the nature of an afterglow with continuous radiation. The effects of premixing oxygen, nitrogen dioxide, or nitric oxide with the methyl nitrate vapour were observed. Both oxygen and nitrogen dioxide converted the orange red afterglow into a brighter and better defined reaction zone but the spectra of the flames were not affected and there appeared to be no significant effect of the additives on the flame speed. Nitric oxide had no effect at all. The structure of the flame could be simulated by burning mixtures of methyl nitrite and oxygen.

These authors also discovered that methyl nitrite would support a decomposition flame at atmospheric pressure. The reaction zone was orange and weak in intensity and was surmounted by an even feebler orange afterglow. Formaldehyde vapour was produced which condensed on the cooler parts of the burner. The flame did not propagate in a tube of less than about 2 cm diameter and its speed was very low, about 2 to 3 cm/s. It did not burn at reduced pressure, unless the combustion was assisted by the admixture of oxygen.

The observations on the stationary low pressure flame of methyl nitrate which are compatible with the view accepted for the thermal decomposition, namely, that fission of the O—N bond occurs first, may be generally explained on the basis of two established facts: (*1*) that the ester undergoes extensive pyrolysis before the main reaction zone, and (*2*) that nitric oxide is very stable and will only react at high temperatures and pressures. An attempt to decide the rate-controlling reaction in methyl nitrate and ethyl nitrate flames was made by G. K. ADAMS and J. SCRIVENER[26], who measured the speed of flame propagation in each and in mixtures of the two with and without the addition of inert gases. The influence of the diluents showed that flame temperature was the most important factor affecting flame speed. The latter did not depend directly on the partial pressure of the methyl nitrate and hence the reaction is second order with respect to the reactants. By employing Semenov's expression for the derivation of a flame velocity in a second order reaction these authors found that the activation energy for the rate-controlling step would be about 22 kcal/mole which is much too low to be identified with the reaction

$$CH_3O{-}NO_2 \longrightarrow CH_3O + NO_2 \quad E \sim 35 \text{ kcal/mole} \qquad \ldots [9]$$

but might correspond with reactions involving nitrogen dioxide

$$\text{e.g. } NO_2 + CH_2O \quad E = 19 \text{ kcal/mole} \qquad \ldots [10]$$

$$NO_2 + NO_2 \quad E = 25 \text{ kcal/mole} \qquad \ldots [11]$$

The decomposition flame of ethyl nitrate has been investigated also. H. THEILE[27] obtained the flame on the surface of the liquid in a capillary tube and found that the combustion was very incomplete. H. G. WOLFHARD[28] examined the explosive decomposition of the vapour in a tube

8 cm in diameter and 140 cm long at pressures between 6 mm and 200 mm of mercury. At the lower pressure the flame was invisible in daylight but its path was marked by the formation of a smoke cloud which was found to consist of particules of paraformaldehyde, and the walls of the tube were coated with this compound after a few explosions. In a darkened room the flame could be seen as a single grey reaction zone and at higher pressures a second zone appeared. Wolfhard was able to obtain a stationary flame by passing the vapour through a conical tube and igniting it with a spark at the wider top end. The flame which was in the form of a flat disc travelled down the converging tube until it found a position where the flame velocity matched the flow velocity of the vapour. Rough values of the burning velocity (S_u) were obtained and shown to be low (about 7 cm/s) and unaffected by pressure. The quenching diameter (Q_u) is also small and the product ($S_u \times Q_u$) which is related to the temperature in the flame front at which reaction starts is remarkably small indicating that reactions occur under conditions which would quench reactions in flames supported by oxygen. The measured temperature of the flame based on the strength of the absorption bands of nitric oxide gave a value of only 460°C.

An attempt to determine the chemical reactions in the ethyl nitrate flame was made by D. P. NEEDHAM and J. POWLING[29] who established a stationary flame on the liquid at 1 atm pressure. They measured the temperature through the flame with a thin Pt/Pt–Rh thermocouple sheathed with Pyrex and with the aid of a thin silica probe took samples of the products at different heights above the surface. The samples were analysed by a combination of i.r. and chemical techniques. On plotting the temperature against the height above the surface the authors found an inflection or pause in the rate of temperature rise at 1·5 to 2 mm where the temperature was about 1 060°K and this point of inflection was also detected by shadowgraph. Very rapid changes of composition occur in the flame front and within 0·5 mm of the liquid surface the chief products were water, nitric oxide, carbon monoxide and formaldehyde in nearly equimolecular proportions together with acetaldehyde and very much smaller concentrations of methane and hydrogen.

Needham and Powling consider that the initiating reactions which are not rate-determining probably correspond to those established for the thermal decomposition, viz.

$$CH_3CH_2ONO_2 \longrightarrow CH_3CH_2O + NO_2 \quad \ldots\ldots [12]$$

$$CH_3CH_2O \longrightarrow CH_3 + HCHO \quad \ldots\ldots [13]$$

An additional primary step is suggested

$$CH_3CH_2ONO_2 \longrightarrow CH_3CHO + HONO \quad \ldots\ldots [14]$$

and reaction 13 may have a competitor in reaction 15 below

$$CH_3CH_2O \longrightarrow CH_3CHO + H \quad \ldots\ldots [15]$$

The products found by analysis cannot be explained on the basis of subsequent reactions between nitrogen dioxide and organic fragments and the authors believe that the mechanism is chain thermal, the ethyl nitrate being burnt mainly by reactions with nitrogen dioxide and nitrous acid which are chain carriers.

$$NO_2 + CH_3CH_2ONO_2 \longrightarrow HONO + [C_2H_4ONO_2]$$
$$\downarrow$$
$$CH_3CHO + NO_2 \text{ or } 2HCHO + NO \quad \ldots . [16]$$

$$HONO + CH_3CH_2ONO_2 \longrightarrow H_2O + NO + [C_2H_4ONO_2] \quad \ldots . [17]$$

These and other reactions postulated by the authors account for the products. The important thing is that these reactions are exothermic and do not depend on heat liberated by reactions occurring later in the flame.

J. POWLING and W. A. W. SMITH[30] examined *iso*propyl and *n*-propyl nitrate by a similar method in order to find the effect of molecular structure on the mode of degradation in decomposition flames and found that the mechanism postulated for ethyl nitrate held for the higher members of the series. Again recombination of alkyl radicals with nitrogen dioxide is thought to be less probable at elevated temperatures in the flame than chain reactions analogous to those given above for ethyl nitrate.

R. STEINBERGER, C. A. ORLICK and V. P. SCHAAF[31] made burning rate studies with deuterated liquid nitrates in order to study the role of atomic hydrogen in the flame and as a result believe that the following reaction is important

$$H + RR'CHONO_2 \longrightarrow H_2 + RR'\dot{C}ONO_2 \quad \ldots . [18]$$

Methyl nitrite

It has been mentioned already that methyl nitrite vapour can be burnt as a decomposition flame at atmospheric pressure. This flame is of particular interest because it depends upon the reduction of nitric oxide for its existence yet the temperature is such that no thermal decomposition of nitric oxide is likely to occur. Detailed studies have been made by P. GRAY and M. W. T. PRATT[32] and by E. A. ARDEN and J. POWLING[33]. The former authors established a diffusion flame of methyl nitrite in air on a tube a few centimetres in diameter. This flame had an inner zone which was orange red in colour and on reducing the vapour flow this zone descended the tube as a flat disc surmounted by a feeble afterglow of the same colour, while downstream a white polymeric deposit with a strong odour of formaldehyde formed on the walls. The flame velocity inside the tube was about 3 to 4 cm/s for vapour initially at 18°C and the velocity increased to 7 to 8 cm/s when the vapour was preheated up to 240°C. No decomposition flame could be obtained if the vapour was preheated above 240°C, however.

Arden and Powling obtained the decomposition flame as a flat disc on top of a burner 3·5 cm in diameter. The flame which was nearly invisible was detected by a shadowgraph. From the measured temperature profile and the products of analysis of samples withdrawn through a fine silica

probe placed at different heights above the burner it was found that the decomposition was complete below 700°C at which point there was an inflection in the temperature profile. The overall reaction at this stage is represented by

$$CH_3ONO \longrightarrow \underset{19\%}{\tfrac{1}{2}CH_3OH} + \underset{20\%}{\tfrac{1}{2}CH_2O} + \underset{42\%}{NO} \qquad \ldots . [19]$$

which is nearly thermoneutral. An exothermic reaction then proceeds between nitric oxide and the other products of the reaction to produce water and nitrogen but the reaction does not proceed after degradation of the methanol and formaldehyde to carbon monoxide and hydrogen. This process appears to be complete at about 9 mm from the flame front and about 50 per cent of the nitric oxide remains unchanged at a final temperature of 1 100°C.

The initial step in the decomposition is most likely to be

$$CH_3ONO \longrightarrow CH_3O + NO \qquad \ldots . [20]$$

because the O—N bond is the weakest in the molecule and also the presence of methanol in the products would be difficult to explain otherwise. This reaction which has an activation energy of 38 kcal/mole is not rate-controlling, however, but the succeeding steps are uncertain. Reactions between nitric oxide and free radicals which were mentioned in connection with hydrocarbon flames supported by nitric oxide probably play a part, and Arden and Powling suggest that H atoms produced on pyrolysis of methanol and formaldehyde may react

$$H + NO \longrightarrow HNO \qquad \ldots . [21]$$

Halogen flames

Lastly mention must be made of the properties of some very interesting flames supported by the halogens. The extreme reactivity of fluorine with which many substances including water will burn is well known and so also is the inflammable nature of the other halogens. It is only comparatively recently, however, that spectroscopic, kinetic and flame-inhibiting studies have been made with the aid of stationary flames.

R. A. DURIE[34] examined small diffusion flames of fluorine with a wide range of fuels and obtained the spectra. G. SKIRROW and H. G. WOLFHARD[35] using mainly chlorine trifluoride greatly extended this work but again confined it to diffusion flames because of the difficulties of premixing gases with fluorine. A. V. GROSSE and A. D. KIRSCHENBAUM[36], however, found that after eliminating impurities, especially hydrofluoric acid and certain metals, fluorine could be mixed with hydrogen provided each gas was precooled to 90°K beforehand and the temperature of the mixture was not raised above 195°K in Pyrex apparatus. Mixtures in the range 6 to 25 per cent by volume of fluorine were burnt without detonation on the tip of a burner and the burning velocity was estimated from the height of the cone, which was clearly defined and pale pink. The values obtained were ten times greater than those of mixtures of hydrogen and oxygen with the same equivalence ratios. Stoichiometric mixtures could

not be burnt without detonation but extrapolation of the results for lean and rich mixtures indicated a burning velocity of 10^4 cm/s.

Chlorine is a more manageable oxidizer and premixed and diffusion flames have been burnt with hydrogen and hydrocarbons[37–39]. Bromine is still less reactive and although hydrogen burns readily in it, hydrocarbons are reluctant to burn and interest centres more on the remarkable inhibiting effect of bromine on air flames[10, 41]. There is no recent work to report on iodine although a sodium–iodine flame was investigated about thirty years ago[12].

A comprehensive account of the structure and light emission of halogen flames is given by R. F. SIMMONS and H. G. WOLFHARD[13]. Hydrogen diffusion flames are as featureless as those of hydrogen and oxygen, and emit only a strong continuum which is attributed to the recombination of halogen atoms. With hydrocarbons, however, the flames differ considerably from those supported by oxygen particularly with respect to greater carbon formation. Even in diffusion flames with air an enhancement of the luminous zone can be seen as soon as a halogen is introduced. When all the air is replaced by fluorine or chlorine, however, the carbon formation is very pronounced. The carbon zone is no longer separated from the main reaction zone and it seems that carbon formation by pyrolysis of the hydrocarbon is being augmented with carbon formed in hydrogen abstraction processes by halogen diffusing into the carbon zone. A notable consequence is that heat losses by radiation are considerable and the flame temperatures are much below the theoretical.

The addition of a hydrocarbon to the hydrogen of a hydrogen–fluorine diffusion flame produces a very interesting change in structure. On the fuel side a carbon zone appears and between this and the main reaction zone which is grey there appear green, blue, and red zones which are due to the emission bands of C_2, C_3, CN and CF. The presence of these radicals suggests that the fluorine does not penetrate into this part of the flame but reacts with hydrogen which diffuses more rapidly than the radicals into the fluorine stream. This suggestion is supported by the effect of adding a little oxygen to the fluorine when OH bands appear on the fluorine side and the emission of the C_2 and CN bands is diminished and accompanied by the appearance of CH bands.

As with oxygen flames important differences exist between the characteristics of premixed and diffusion flames. R. F. SIMMONS and H. G. WOLFHARD[39] examined a premixed flame of ethane and chlorine. In very fuel-rich flames the inner cone is dull red and the temperature is quite low so that excess fuel does not decompose and carbon formation is slight. As the composition approaches the stoichiometric, however, the flame becomes bright yellow and produces large quantities of soot. The temperature is well below the theoretical because of heat losses by radiation. Towards the lean limit the flame temperature is again low and carbon formation ceases but stable carbon compounds such as hexachlorethane can be detected. These flames only emit a continuum and neither C_2 nor CH is observed even when carbon formation ceases. Burning velocity measurements which were attempted by the bunsen cone method gave

results of the order of 5 cm/s even for stoichiometric mixtures and these low values contrast with a value of about 400 cm/s which Bartholomé[38] measured in premixed hydrogen–chlorine flames.

Premixed flames of hydrogen with bromine have been studied experimentally by R. C. ANDERSON and co-workers[44]. This system has aroused considerable interest because the energy involved is relatively low and the theoretical maximum flame temperature is not above about 1 400°C. Moreover, it is a chain reaction about which there is detailed information and it is considered an ideal flame for the application of rigid flame equations and for studying the significance of simplifying assumptions which render the equations capable of solution. Interesting theoretical studies of this kind have been made by E. S. CAMPBELL[45], and by M. GILBERT and D. ALTMAN[46].

CONCLUSION

Air flames on account of their wide application have dominated combustion research hitherto. This brief review indicates that self-propagating flames are not confined to oxidation reactions by oxygen or even to oxidation reactions in the broadest sense. Interest in these unusual flame reactions is growing and more systems have been studied than could be considered here. Notable omissions are work on ozone[47], on ethylene oxide[48–50] and on organo-metallic self-propagating flames[51] all of which have aroused considerable interest because of the associated theoretical work on the prediction of burning velocities. Investigations of the newer systems have benefited greatly from the techniques developed for research on air flames and it is to be hoped that the fresh knowledge which is resulting will prove to be a significant contribution to the understanding of the phenomenon of flame.

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Recent Developments and Notes

PREHEATED COMBUSTION AIR

E. H. HUBBARD, principal investigator at the IJmuiden Experimental Station of the International Flame Research Foundation, has recently published a paper describing trials carried out on the new oil and gas furnace during which the effect of preheated combustion air on flame propagation was studied [*J. Inst. Fuel* 30 (1957) 564]. The results show that using hot combustion air makes little difference to the mixing pattern, to the carbon formed in the flame and to the emissivity, the increase in radiation being solely due to the higher gas temperatures, which are of the order of 26°C for each 100°C of air preheat. The formation of carbon particles in oil flames by hydrocarbon cracking occurs very quickly and the main effect of changing the type of fuel, thrust, combustion air quantity and temperature, is on their rate of burning out. At the temperatures considered, about 1500°C, this is only altered by the mixing history and not by the flame temperature.

CARBON–OXYGEN REACTION AT HIGH TEMPERATURES

A conference organized by the Society of Chemical Industry on *Industrial Carbon and Graphite* was held in the William Beveridge Hall of the University of London, on 24 to 26 September 1957. Sixty six papers were presented by scientists from a dozen countries. R. J. DAY, P. L. WALKER, Jr. and (the late) C. C. WRIGHT, of the Pennsylvania State University, gave an account to the conference of their work on the carbon–oxygen reaction under high temperature and high gas velocity conditions. High-velocity technique was used in an attempt to remove as far as possible the effects of diffusional films and interfering secondary reactions on the kinetics of the overall carbon–oxygen reaction. They found that the rate of combustion of petroleum coke carbon increased proportionally with the square root of the gas injection velocity at carbon surface temperatures of 1500° and 2000°K. The rate of carbon consumption was shown to be directly proportional to the oxygen concentration from 37 to 100 per cent in oxygen–nitrogen mixtures, at all temperatures studied. The apparent activation energy for the combustion of the carbon decreased from 5·3 to 2·3 kcal/mol as the gas injection velocity increased from 5 000 to 60 000 ft/min. Nitrogen, helium, carbon monoxide and carbon dioxide were found to act merely as diluents during combustion, water vapour decreased the product CO/CO_2 ratio, and chlorine strongly retarded the combustion reaction. The results indicate the importance of using a high gas-injection velocity if rapid combustion rates of carbon are desired.

GASEOUS DETONATION

Some new phenomena have been revealed in an investigation on the mechanism of the initiation and the structure of detonation waves carried out by B. GREIFER, J. C. COOPER, F. C. GIBSON and C. M. MASON, of the

U.S. Bureau of Mines, Division of Explosives Technology, Bruceton, Pennsylvania [*J. appl. Phys.* 28 (1957) 289].

The streak schlieren technique was used and photographs were obtained of hydrogen–oxygen and carbon monoxide–oxygen explosions in a rectangular detonation tube. The details of detonation wave structure as shown on the photographs confirm existing views as to the initiation of detonation. In the early stages of propagation of a combustion wave, compression waves are generated and soon steepen into a shock wave which travels ahead of the combustion wave, that is, the zone of chemical reaction. This combination of shock and combustion waves is characteristic of a non-steady detonation state in the moments before stable detonation is initiated. The distance between the two waves narrows as the explosion progresses down the tube due to the formation of new combustion centres ahead of the combustion wave by means of auto-ignitions. Eventually the combustion wave overtakes the shock wave and supplies it directly with energy from the chemical reaction; at this moment stable detonation is initiated.

Several groups of striations seen on these records are known to be characteristic of stable detonation, for example, horizontal striations which are associated with the phenomenon of spinning detonation in carbon monoxide–oxygen mixtures. Amongst new features of the records obtained in the present investigation are *retrograde* striations which travel from the detonation front but in the direction opposite to that taken by the front. It is suggested that these may be miniature detonation waves arising from some mechanism of discontinuous propagation of the detonation, undetected until now because of the very high frequency and small amplitude of the velocity change involved.

COMBUSTION OF LEAN GASES

The successful application of gas of extremely low thermal value for heating at a large Russian chemical plant has been described by L. B. AVETISYANTS and S. N. SHORIN [*Gaz. Prom. (Gas Ind., Moscow)* (1957) (4) 22; see abstract in *Chem. Abstr.* 51 (1957) 11 693]. There is increasing importance now attached to industrial heating by the use of gases with calorific values in the range of 100 to 300 kcal/m^3, such as water gas, hot blast from coke and anthracite and exhaust gases from internal combustion engines. The thermochemistry of such fuels and the design of special burning equipment for their use are now being studied. In the present case the hot blast from a water gas set with average contents of carbon monoxide and hydrogen, 7·2 and 2·0 per cent respectively, at a temperature of 560°C and a Q value of 266 kcal/m^3 (29 B.Th.U./ft^3) has been employed successfully by means of contact catalysis and the use of preheated air. The gas–air mixture (coefficient of excess, 1·08) at a temperature of 790° is completely burned in passing a contact bed 350 mm deep consisting of lumps of refractory grog 30 to 40 mm in diameter to generate a bed temperature of 1 160°C. Gas consumption is 2 600 m^3/h and the heat output at the bed is $2{\cdot}7 \times 10^6$ kcal/m^2/h.

HYDROGEN PEROXIDE AS A MISSILE PROPELLANT

Until quite recently hydrogen peroxide of 90 per cent by weight was the highest concentration available in quantity. In 1955, however, the Becco Chemical Division of Food Machinery and Chemical Corporation announced the availability of tonnage quantities of hydrogen peroxide in concentrations up to 99·7 per cent or virtually anhydrous. The first commercial-scale process for the production of hydrogen peroxide of such concentration has now been described by R. BLOOM, Jr, and N. J. BRUNSVOLD, of the above Corporation [*Chem. Engng Progr.* 53 (1957) 541]. The properties of the product are discussed and particularly its application in the field of missile propellants.

The manufacturing process depends on concentrating hydrogen peroxide solutions and the freezing properties of these solutions are used to accomplish fractional crystallization. Anhydrous hydrogen peroxide has the characteristics which make 90 per cent hydrogen peroxide systems with catalytic decomposition reliable and simple. Added advantages are greater density and greater heat of decomposition than with the 90 per cent concentration, and these tend to increase the energy output per unit weight and the volume of gas produced on decomposition. The temperature of decomposition is 1 000°C as compared with 750°C for peroxide of 90 per cent concentration. The anhydrous material has the disadvantages of a higher freezing point and slightly decreased thermal stability, but these can be overcome in particular cases by engineering devices.

PREFLAME REACTIONS IN A MOTORED ENGINE

The preflame reactions in the end-gas region in spark ignition engines are regarded as being intimately concerned with the phenomena associated with knock. Many experimental methods have been developed in recent years for studying these reactions in order to elucidate the fundamental nature of knock. Much of the available information concerning the identities and concentrations of some of the reactants taking part in the pre-knock reactions has been obtained by using a variety of gas-sampling techniques. This approach, however, is subject to considerable limitations inherent in the sampling operation. Recently spectrometric analysis of the reacting mixture in the combustion chamber has been applied and a paper by K. J. PIPENBERG and A. J. PAHNKE, of E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., describes their spectrometric investigations of n-heptane preflame reactions in a motored engine [*Industr. Engng Chem. (Industr.)* 49 (1957) 2067].

A spectrometer covering the wavelength range from 0·3 to 15 microns was used in conjunction with an ASTM supercharge method engine which was motored under increasingly severe operating conditions. The pale blue luminescence, associated with cool flame radiation, in an early stage of the preflame reactions and a bright blue flame at a later stage were the particular phenomena of study in this research. Actually three distinct radiation phenomena, cool flame, blue flame, and intense blue flame, are referred to as being experimentally observed. The results obtained are

said to be evidence that the preflame reactions progressively involve more extensive degradation and oxidation of the fuel. Hydrocarbon decomposition and the formation of carbonyl compounds are believed to be involved in reactions emitting cool flames and further oxidation of these compounds is especially important in the reactions giving blue flames. Free radical reactions occurring under the conditions for formation of the intense blue flames easily lead to auto-ignition and knock. Tetraethyl lead apparently functions by slowing down carbonyl decompositions under blue flame conditions, perhaps by deactivating free radical intermediates.

SECOND CONFERENCE ON PULVERIZED FUEL

In June 1947 there was held at Harrogate a conference arranged by the Institute of Fuel to consider the use of pulverized fuel. A review of developments that have taken place in pulverized fuel firing since then has formed the subject of the recent Second Conference held by the Institute in London, on 27 to 28 November 1957. At two sessions the papers presented dealt with fundamental and applied research, at another session the subject was pulverized fuel practice in the United Kingdom, and at the final session practice in Australia, France, Belgium, Germany and the United States of America.

Amongst the papers dealing with fundamental research three were presented on different aspects of the combustion of pulverized fuel. These were by R. H. ESSENHIGH, on burning times of coal particles in a pulverized fuel furnace, T. J. PEIRCE and M. W. THRING, on the distribution of residence times in a model of a pulverized fuel boiler, and M. W. THRING and E. H. HUBBARD, on the radiation from certain pulverized fuel flames.

The objective of the work described by R. H. ESSENHIGH, Central Electricity Authority Research Fellow in the University of Sheffield, was to compare the burning times of coal particles measured in the laboratory with those of the same coal measured in the experimental pulverized fuel furnace used in the work of the International Flame Research Foundation at IJmuiden. Ignoring at first the effect of volatile matter, and using a square law equation found experimentally by observing the burning times of single captive particles of coal, an equation for burning times in a flame was derived which has the form

$$t_c = F - Kd_0^2$$

where t_c is the burning time, F is a complex function of excess air, d_0 is the initial diameter of the coal particle, and K is a burning constant which is determined experimentally. This equation is shown to differ from the equation for a single particle only by the introduction of the multiplying factor F. The effect of volatile matter is to reduce the oxygen concentration and in calculating the residue burning time this can be allowed for by introducing an additional factor. Comparison between predicted and experimental values of residue burning times for the coal used in the experimental furnace shows a reasonable order of magnitude agreement. In view of this the equation is put forward as a semi-empirical one which

may be of practical value in the design of furnaces and boilers. Measured volatile burning times do not agree with the theory.

RESIDENCE TIMES OF COAL PARTICLES IN A PULVERIZED FUEL BOILER

A paper presented to the Second Conference on Pulverized Fuel (see previous note) by T. J. PEIRCE and M. W. THRING described experimental work carried out in the University of Sheffield, dealing with the distribution of residence times of coal particles in a pulverized fuel boiler. As some particles travel straight through the chamber and others recirculate within it, a knowledge of the residence time distribution function is important because it enables burning times to be matched to residence times. An equation for this function was tested experimentally on a one-twentieth full-size model of a furnace operated isothermally. This was constructed on the basis of geometric and dynamic similarity with the full-scale combustion chamber, together with the introduction of a criterion to compensate for the non-isothermal operation of the boiler. In this way a satisfactory representation is obtained of the full-scale aerodynamic conditions. A known weight of lycopodium powder, used as a tracer, was injected through one of the burners, and metered at the chamber outlet by interrupting a beam of light falling on to a photocell. For three methods of firing, burner nozzles horizontal, tilted 30° up and tilted 30° down, the form of the distribution equation is the same, but the constants are different. For horizontal firing there is close agreement between the measured value of mean residence time and a calculated mean time

$$T_m = V/Q$$

for the air flow where V is chamber volume and Q is the total flow rate through the model. For the burner tilted up the measured time was less than T_m, indicating uneven distribution of air throughout the chamber, and for the burner tilted down, the measured time was longer than T_m, perhaps because of relative velocity between particles and air.

DEVELOPMENTS IN PULVERIZED FUEL FIRING OF BOILERS

W. G. MARSKELL, of Babcock and Wilcox Ltd, presented a paper to the Second Conference on Pulverized Fuel (see previous notes) in which were reviewed developments in boiler firing during the past ten years. He regards the most outstanding development as being probably the very rapid expansion of cyclone firing in America and Germany. The first commercial cyclone-fired boiler was installed in Chicago in 1944 and at the present time there are sixty nine cyclone-fired boilers, on order or operating, in the U.S.A. These cyclones are mostly fired with coal crushed to pass $\frac{1}{4}$ in. screen, and the fuel is injected on the axis of the cyclone. In Germany the first cyclone-fired installation was at Düsseldorf Power Station in 1950. As the American system of firing presented difficulties with the German coals used, a change-over was made to coarsely pulverized fuels, injected tangentially into the periphery of the cyclone. At the present time only one cyclone-fired boiler is in operation in the U.K. and this is tangentially fired with coarsely pulverized coal on the German system. A second boiler

designed for axial firing on the American system is about to be commissioned at the Barking Station of the Central Electricity Authority. The relative merits, therefore, of these two systems will eventually be capable of assessment under British conditions. Three other cyclone-fired boilers are under construction or on order in the U.K. These are all tangentially fired.

R. F. DAVIS, International Combustion Ltd, read a paper to the same Conference on developments in large pulverized fuel-fired boilers during the past ten years. It is pointed out that it is the inert constituents of pulverized coal that present the real problem in its use and in Central Europe this problem has become acute and various designs of slag tap and cyclone furnaces have been devised to overcome it. In the United Kingdom, however, a very good performance has been achieved with the dry-ash furnace.

A notable improvement in combustion technique in the period under review has been the introduction of the tilting corner burner. Another feature that has been introduced is the platen superheater, consequent upon the increase in steam temperature and the use of poorer quality coals. The high gas temperature entering the superheater may often be higher than the softening temperature of the coal ash, a condition which may lead to serious build-up of deposits, especially with high-chlorine coals. The platen superheater absorbs heat mainly by gas radiation from the thick gas layers between the heating surfaces and the gas temperature is reduced on its path through them. Reference is also made to the use of radiant superheaters and the newest development with assisted boiler circulation in later designs.

Development and trends in pulverized coal firing in Germany were discussed in a paper by W. GUMZ, of Steinkohlenbergbauverein, Essen. At present over 50 per cent of the steaming capacity of larger power stations in Germany depends on pulverized fuel firing. During the last decade more than two hundred slagging furnaces have been installed and put into operation. Slagging furnaces with bituminous coal and dry-bottom furnaces at low-temperature combustion with brown coal are preferred because they ensure easier handling, storage and utilization of slag. When fly-ash sintering processes are available and provide a reliable technique for fly-ash processing, dry-bottom furnaces will be favoured to some extent because of better boiler availability and easier operation.

AMERICAN RESEARCH ON FLAMES AND EXPLOSIONS

The *Report of Research and Technologic Work on Explosives, Explosions and Flames, Fiscal Years 1953 and 1954*, compiled by RUTH F. BRINKLEY and R. W. VAN DOLAH, is available (*Inform. Circ. U.S. Bur. Min. No. 7804*, November 1957). This is sixteenth in a series of reports originally issued annually and more recently biennially describing the work of the Division of Explosives Technology of the Bureau of Mines. In the majority of instances the results of the investigations are made available through official publications and journal articles, but in addition there are summaries of tests of explosives, hazardous chemicals and dusts.

Amongst the investigations on the flammability of gases and vapours, some of the problems encountered in combustion at high altitudes, that is, at low temperatures and pressures, have been examined. Flammability studies of complex hydrocarbon fuels have been made over a wide range of temperatures and pressures and have shown that certain factors, unimportant at ordinary temperatures and pressures, become important at low temperatures and sub-atmospheric pressures. In designing apparatus for determining limits of flammability under these conditions, special consideration must be given to the size and shape of the test chamber and to the source of ignition. Combustible liquid mixtures must be handled with care before testing to prevent loss by vaporization of highly volatile constituents that play a negligible part at higher temperatures but may be very important at low temperatures and pressures.

During the period under review about fifteen major gas and dust explosions were investigated. More than 3 000 doctors, nurses and other hospital personnel witnessed demonstrations of static electricity hazards as related to explosions of anaesthetic gas in surgical operations.

INTERNATIONAL RESEARCH ON FLAME RADIATION

Shortly after the end of the 1939–45 war a programme of research into heat transfer by radiation from flames was initiated at The Royal Netherlands Blast Furnace and Steel Works at IJmuiden. International cooperation in the work began when France and England shortly afterwards began to contribute both financially and by way of planning and execution of the experiments. In 1952 an American committee, under the chairmanship of Professor H. C. HOTTEL, was formed for cooperation in the work, and these countries have now been joined by Belgium, Sweden and the High Authority of the European Community of Coal and Steel. In November 1955, the International Joint Committee for Flame Radiation was formalized by its registration in Holland as the International Flame Research Foundation. The president of the Foundation is Professor G. M. RIBAUD and the general superintendent of the research programme, Professor M. W. THRING, of the Department of Fuel Technology and Chemical Engineering, University of Sheffield.

Full accounts of the progress and results of the work have been published from time to time in both England and France, but until recently there has been no comprehensive account given in the U.S.A. R. A. SHERMAN, Technical Director, Battelle Memorial Institute, Columbus, Ohio, a member of the Joint Committee governing the Foundation, has now published a summary of the work and discussed some of the results [*Trans. Amer. Soc. Mech. Engrs* 79 (1957) 1727].

In the work at IJmuiden the emissivities and temperatures of the flames are derived by the Schmidt method [H. SCHMIDT, *Ann. Phys., Lpz.* 29 (1909) 971]. The author of the present paper questions the validity of this method applied to these flames and considers the emissivities and temperatures derived in this way as only approximate. He points out that the Schmidt method is applicable only to grey flames; for non-grey flames,

such as non-luminous flames, it is true only when the temperature of the wall is equal to the temperature of the flame, which is not usually so. In the discussion on the paper when it was presented to the annual meeting of the American Society of Mechanical Engineers in November 1956, Professor THRING stated that the applicability of the Schmidt method to their flames had been checked. In the regions where the flame was luminous there did not appear to be a significant error due to the background temperature differing from the mean radiant temperature of the flame. He agreed that there would be appreciable error in the non-luminous tail of the flame. In the luminous regions the non-uniformity of temperature through the flame obscures the errors due to the inequality of flame and background temperature.

INFLAMMABILITY LIMITS OF GASES

Sir ALFRED EGERTON pointed out in a recent paper that a satisfactory theory of flame propagation should be able to predict: (*a*) the fact that below certain concentrations of combustible or oxygen flame will not be propagated, (*b*) the lower limit of concentration, and (*c*) the burning velocity at the limit (*Fourth Symposium on Combustion, 1953*, p 4; Baltimore: Williams and Wilkins). A theory of this kind has now been put forward by D. B. SPALDING, of the Imperial College of Science and Technology, London [*Proc. Roy. Soc. A* 240 (1957) 83]. The new feature presented is that heat exchange between the gas and its solid surroundings is considered, and this process appears to be able to account for the existence and nature of inflammability limits. It is shown that even if the bounding walls of the gas are too far away for conductive heat loss to be effective, gas radiation can have sufficient effect. It is demonstrated that a given combustible mixture has two possible burning velocities of which only the upper one is stable in usual circumstances. At the limits of inflammability the two velocities coincide, while outside the limits they are imaginary, that is, when the reaction rate is too low compared with the rate of heat loss. A result of the theory is to bring the laminar one-dimensional flame into line with other flames, for example, the homogeneous steady-flow reaction zone, the solid-fuel surface, and the gaseous diffusion flame, each of which shows a zone of stable operation limited on the one hand by chemical reaction rate and on the other by heat losses to the surroundings.

COMBUSTION OF HYDROGEN SULPHIDE

Using the method of kinetic spectroscopy and flash photolysis R. G. W. NORRISH and A. P. ZEELENBERG, Department of Physical Chemistry, University of Cambridge, have investigated the combustion of hydrogen sulphide [*Proc. Roy. Soc. A* 240 (1957) 293]. It was found that if no large excess of inert gas was present the reaction produced sulphur dioxide. The reaction was shown to take place in steps in which the radicals SH and OH participate. Simultaneously with the appearance of the sulphur dioxide a light emission was observed which is attributed to the process

$$SO + O \rightarrow SO_2 + h\nu$$

In the presence of a large excess of inert gas the reaction results in S_2O_2. The formation of this compound is favoured by low temperature.

SPONTANEOUS COMBUSTION OF COAL

A monograph, *Research on Spontaneous Combustion of Coal in Mines, A Review*, has been published by H. F. COWARD (Ministry of Power: *Safety-in-Mines Res. Rep. No. 142*: September 1957). This is a comprehensive review of laboratory investigations on the circumstances in which spontaneous combustion of coal may occur, particularly in mines.

The spontaneous combustion of coal was at first attributed to the oxidation of pyrites by air, but by 1870 or so it was becoming clear to investigators that coals on exposure to air underwent chemical change which pointed to the oxidation of the coal substance as the cause of self-heating. The 'pyrites theory' was abandoned but later many experimenters have accepted the view that some small contribution may be made by pyrites to the heat developed on oxidation of a pyritic coal.

The nature and precise site of the reaction between oxygen and the coal substance are still obscure. The chemical reaction is concluded to have few, if any, close parallels among other oxidation processes. It occurs on the exposed surface of the coal, but only within millimetres or perhaps a very few centimetres of the surface. The recognition a few years ago of the formation of 'peroxygen' on the surface of coal exposed to air gives importance to the search for an oxidation inhibitor which might destroy the chain-carrier 'peroxygen' and so counter the danger of spontaneous combustion in coal mines. There are many aspects of the subject that require elucidation, such as the nature of the coal, the right particle size and minimum quantity of it, and the right rate of aeration which at 20° to 40° C would lead to spontaneous heating in air. In addition, there are the problems connected with the presence of pyrites.

ROYAL SOCIETY OF ARTS: PRIZES

The Royal Society of Arts is the Trustee for certain endowments and in connection with them offers prizes during 1958. The *Howard Prize* of £50 will be awarded to the author of a treatise on some aspect of the subject of motive agents. The *Fothergill Prize* of £20 is offered for a descriptive essay or model embodying some new idea for the prevention or suppression of fire. Entries for these prizes must be received by the Secretary of the Royal Society of Arts, 6–8 John Adam Street, Adelphi, London, W.C.2, not later than 31 July 1958, and must be clearly marked with the entrant's name and address and the prize for which they are submitted. Essays must be typewritten. Entries for these awards may be made by persons of any nationality. Further particulars may be obtained from the Society.

The *Howard Prize* for 1957 was awarded to A. E. JOHNSON, of the Mechanical Engineering Laboratory, East Kilbride, for a treatise on 'Turbine disks for jet propulsion units: an account of work of the Disk Panel of the Ministry of Supply, Gas Turbine Collaboration Committee, during the years 1941–49'.

The *Fothergill Prize* for 1957 was awarded to P. B. SMITH, of the Safety in Mines Research Establishment, Buxton, for an essay on 'A new method of suppressing fires in mines'.

DESIGN OF TURBOJET COMBUSTORS

A quantitative contribution to the subject of turbojet combustor design has been made in a paper by J. S. GROBMAN and R. T. DITTRICH, National Advisory Committee for Aeronautics, Lewis Flight Propulsion Laboratory, Cleveland, Ohio, with C. C. GRAVES, Nuclear Development Corporation of America, White Plains, N.Y. [*Trans. Amer. Soc. mech. Engrs* 79 (1957) 1601]. In this paper they describe the development from theoretical calculations of generalized curves showing the combustor total pressure-loss coefficient and air-flow distribution for various geometric configurations and operating conditions. The results pertain to combustors having (*a*) constant annulus and liner cross sectional areas along the combustor axis, and (*b*) flush circular holes in the liner walls.

It is shown that the hot-flow pressure loss can be minimized by designing the combustor with a liner to total cross sectional area ratio of about 0·6 and a total liner open-hole area greater than the total cross sectional area. Since the combustor total pressure-loss coefficient increases with combustor reference Mach number, increasing the combustor frontal area would reduce the reference Mach number and further decrease pressure loss.

The results presented indicate the problems associated with future combustor designs. The future trend as regards combustors for engines with cooled turbines and new compressor designs will be for operation at higher combustor-exhaust temperatures and higher reference Mach numbers. This, together with the increased liner-hole area required for minimum pressure loss, will tend to decrease the upstream liner air flow. But if the combustion process is to occur in the same upstream region for high-temperature operation as for low-temperature operation, then a larger percentage of air must be admitted into the upstream region. Consequently it would appear that a major problem in combustor development in the future will be the provision of adequate air into the upstream primary combustion zone of combustors without inducing excessive pressure loss.

THE COMBUSTION OF COAL

The Jubilee Memorial Lecture of the Society of Chemical Industry for 1957 was delivered by A. C. MONKHOUSE, Acting Director of the Fuel Research Station, who took for his theme the combustion of coal. This has recently been published [*Chem. & Ind.* (18 January 1958) 52]. The more recent work on the constitution of coal, on the theory of its combustion in fixed beds and in suspension, and the developments in industrial and domestic burning appliances, are reviewed.

With regard to the combustion of the volatile matter from coal which is being burnt in a fixed bed, reference is made to the results of recent investigations in the laboratories of the British Coal Utilisation Research Association and in the University of Sheffield. The initial brown tarry

smoke of distillation of coal is converted into carbonaceous or black sooty smoke, due to the cracking of hydrocarbon molecules. It has been shown that the smoke can be ignited at about 650°C but that if soot particles are allowed to form, higher temperatures in the range of 750°C are required for burning the smoke. The soot particles are more difficult to burn than the tarry particles, not only because a higher temperature is required, but also because the soot particles agglomerate and require a longer time for combustion. The early combustion of the vapours of distillation and the avoidance of cracking of soot to smoke are therefore desirable.

W. A. KIRKBY

FUEL

Attention is drawn to the following *Notes* which were published in the January 1958 issue of *Fuel* and may be of interest to readers of *Combustion and Flame*:

Industrial gas developments

Coke burning appliances

Combustion Institute Interests

SEVENTH INTERNATIONAL SYMPOSIUM ON COMBUSTION, 1958
LONDON AND OXFORD

Readers of *Combustion and Flame* will have already received notice of the Symposium which will take place in London and Oxford (England) from 27 August to 3 September. The main theme of the Symposium will be 'The Physics and Chemistry of Flames'.

It is hoped that visitors will arrive in London on or before the twenty seventh, so that there may be time to see something of London before the opening meeting at 10 o'clock on 28 August at the Royal Institution. The President of the Royal Society will make the opening address. There will be opportunity to visit the combustion laboratories at the Imperial College of Science and Technology in the afternoon. A formal dinner will be held in the evening. The next day the participants will travel to Oxford in the morning and the meetings will be held there during the following days. The Symposium will close after the meeting on Wednesday morning. A visit to Stratford-on-Avon to attend a performance at the Shakespeare Memorial Theatre is being arranged. Other visits will be scheduled during the remainder of the week.

A large number of abstracts of papers which were due on 1 February have been received, and it is hoped that the meeting will maintain the tradition of interest which the previous Symposia in the United States of America have established. Full information is obtainable from the offices of the Combustion Institute, 936A Union Trust Building, Pittsburgh 19, Pennsylvania, or from the Chairman, The Combustion Institute Committee, c/o The Institute of Fuel, 18 Devonshire Street, Portland Place, London, W.1.

WESTERN STATES SECTION (U.S.A.) OF THE COMBUSTION INSTITUTE

The winter meeting took place on 20 January 1958 at the California Institute of Technology, as previously noted in this Journal (page 484, 1957). W. J. BENNET, Chairman of the Section, announced the formal recognition of the Section by The Combustion Institute, following approval of the Section bylaws by the Institute Board of Directors. Officers of the Section, to serve until 1959, are as named in the first report on provisional Section organization (this Journal, page 384, 1957) except that Dr E. E. ZUKOSKI of the California Institute of Technology has been elected Chairman of the Papers Review Committee, to fill a vacancy occasioned by resignation. The next meeting of the Section will be held 23 to 24 June 1958 on the Berkeley campus of the University of California. Programme emphasis will be placed upon combustion of solid and liquid rocket propellants. Deadline for submission of papers is 1 April 1958. It is planned to have a preprint book ready for distribution prior to the meeting. It may be of interest to potential registrants that this meeting has been scheduled to follow immediately the 1958 Heat Transfer and Fluid Mechanics Institute meeting at Berkeley.

Dr A. F. CHARWAT acted as chairman of the morning technical session on 20 January, J. A. DONNELLY in the afternoon, and the abstracts of the six main papers follow.

Studies of diffusion flames, V. Propane, propylene and cyclo*propane diffusion flames*

By S. R. SMITH and A. S. GORDON

We have removed samples of the precombustion products from the diffusion flames of the C_3 hydrocarbons (propane, propylene and *cyclo*propane) with a fine quartz probe. This probe was designed so that the flame was not disturbed, and residence time in the hot section of the probe was sufficiently short to prevent further reaction of the probed sample. The samples probed from the various zones of the flames have been analysed by mass spectrometry and gas chromatography. The analyses of these samples indicate that the mechanism of combustion involves the pyrolysis products at the outer edge of the flame.

The mechanism of the homogeneous pyrolysis in flames of propane, propylene and *cyclo*propane as deduced from the study of the precombustion processes are discussed.

The theory of monopropellant droplet burning

By F. W. WILLIAMS

The steady-state spherically-symmetric burning of a single monopropellant liquid droplet is considered in detail for the case in which a one-step overall reaction of arbitrary order occurs in the gaseous phase following evaporation. Attention is given to the resulting temperature and concentration profiles, the approximate position of the reaction region, and particularly the mass burning rate. An approximate analytical expression for the burning rate is obtained which is valid in the limiting case of large activation energies and for Lewis numbers near unity. This expression indicates that when no mass is internally added to the droplet the square of its diameter decreases linearly with time. The governing equations were integrated numerically for the important case of second-order reactions. It is found that the mass flow rate varies linearly with the droplet radius for large activation energies, but it is proportional to the square of the radius for small activation energies. The later result is peculiar to monopropellant burning and agrees with some recent experiments.

Discussion of halogen flames

By M. GILBERT

Hydrogen–bromine flames have been treated using the kinetics of the classical chain mechanism (KARMAN, PENNER and MILLAN; GILBERT and ALTMAN; *Sixth Symposium on Combustion*. Reinhold: New York, 1956). The chemical-steady-state assumption relative to chain intermediates permitted successful use of the hydrogen bromide global reaction in the flame equations. Good agreement with experiment was obtained, including diffusion.

Some experimental flame speeds are available for hydrogen–chlorine and hydrogen–fluorine flames. Because of the large flame speeds (400 and 2 500 cm/s, respectively) it is of interest to re-examine the considerations governing the chemical-steady-state approximation in these high-speed, high-temperature flames. In very fast flames the 'flow time' becomes smaller than the relaxation time for the controlling intermediate atom reactions. It is therefore expected that the chemical-steady-state should break down completely. Nevertheless, surprising success is obtained in applying the assumption with suitable evaluation of the departure from steady state.

Experimental study of a reverse-jet flame-holder

By G. A. Agoston, A. W. Noon and T. D. Witherly

An experimental study was made of the flow field in the region of flame-holding by a reverse jet. A flame-holding air jet was directed counter to the main stream along the axis of a cylindrical transparent test section. The main stream, a mixture of natural gas and air, entered the test section at uniform velocity. By means of high-speed motion pictures and spark shadow photography, instantaneous observations of the flow fields and flame behaviour were made. Study of these photographic records has yielded significant information relating to jet structure, to the flame-holding mechanism and to flame blowout. From time exposure photographs of the flame, measurements of the jet penetration were made as a function of jet air and main stream flow. In addition, changes in flame envelope configuration were noted as a function of air/fuel ratio as well as the flow rates of the jet and main stream. The influence of non-uniform fuel concentration patterns on flame stability limits was also investigated. This topic was pursued further to include observations of mixing within the flame stabilization region.

The work was supported in part by Wright Air Development Center under contract AF 33(616)–3970.

Some aerodynamic factors influencing bluff body flame stabilization

By F. H. Wright

Bluff body flame-holding experiments have demonstrated that blowoff speed obeys the rule

$$(V_1)_{BO} = (V_1/V_2)(L/\tau)$$

where V_1 is the speed far upstream, V_2 is the flow speed past the wake, L is the length of the recirculation zone and τ is a chemical time parameter. The chemical time is not influenced by the gross fluid dynamic variables, but does depend strongly on such parameters as mixture ratio, mixture temperature and degree of vitiation. On the other hand, the recirculation zone length and the velocity ratio depend on only the gross fluid dynamic variables. Flame-holder blockage has been shown to influence strongly the flow processes and, consequently, to be extremely important in fixing L, (V_2/V_1) and the blowoff speed. Hence, the blockage ratio is one of the more important scaling parameters.

In order to provide a rational basis for prediction of flame-holding characteristics and of the influence of blockage on flame-holding, geometrically simple flame-holders were studied. The flow fields about flat plates oriented normal to the flow in a duct were investigated and the observations were correlated with the flame-holding abilities of the different sized plates. As a guide for this study, a free streamline theory was developed to represent the flow patterns.

Can burner operation

By W. J. BENNET

Four theories of can burner design are discussed and the various empirical correlations examined. Experimental data are presented relating baffle burner design parameters with can burner design parameters. The pilot theory is examined in relation to the spherical reactor work to evaluate burners in terms of maximum space rate. The instantaneous mixing theory is examined and a method of design presented to give a maximum burning rate. The turbulent jet theory is reviewed and test data discussed. Finally, a combined design theory is presented with engineering and powerplant variables considered.

Publications

PRESSURE MEASUREMENT IN VACUUM SYSTEMS

J. H. Leck. London: Published on behalf of The Institute of Physics by Chapman and Hall, 1957. 144 *pp.* 30*s.*

It is very satisfactory for a reviewer to discuss a book about which it is possible to speak as unequivocally as can be done in this case. The subject of low pressure measurement is obviously very important, and the present work is, as claimed by the author, apparently the only one hitherto exclusively devoted to this subject. There are six chapters, which deal with: 1. Mechanical manometers, 2. Thermal conductivity gauges, 3. Ionization gauges, 4. Knudsen radiometer gauge, 5. Surface reaction techniques, and 6. Gauge calibration. The chapter on surface techniques is concerned with various rather special methods which are needed when pressures as low as 10^{-10} mm of mercury are to be measured. The measurement of vapour pressures by means of the effusion method is not dealt with: although not strictly a method of measuring pressure, it would have been interesting and not perhaps inappropriate if this technique had been included.

Each of the principal methods is described in detail, and with considerable clarity, and very full references to the literature are given. The text is fully illustrated with clear figures.

The useful range of pressures and the special characteristics of each gauge are described in the chapter devoted to that gauge: there does not appear to be any point in the book to which one may refer to find out which gauge to use under which circumstances: it is thought that the book would be improved by the addition of a section devoted to this question. Apart from this slight lack, the book is fully recommended as efficiently covering a useful field of scientific measurement.

R. F. Strickland-Constable

PARTICULATE CLOUDS: DUSTS, SMOKES AND MISTS

H. L. Green and W. R. Lane. London: Spon, 1957. *xix* + 425 *pp.* (*illus.*) 70*s.*

The publication of this book by two acknowledged experts in the field is particularly welcome as it is the first comprehensive work since that of Whytlaw-Gray. It is divided into two parts, the first dealing with fundamental physical properties and the second with industrial applications.

The methods of production of particulate clouds are discussed in the early part of the book. These can be considered under two general headings: first, condensation by various means from the gas phase, to give very fine particles; and, second by the production of larger particles by disintegration of liquids and by attrition of solids. Whereas most of the principal methods are mentioned, the coverage of the literature is not by any means complete, and the work of R. P. Fraser and his co-workers is completely ignored.

A comprehensive summary of the physical properties of aerosols then follows and this forms a useful up-to-date account which will be extremely valuable to all workers in the field. Among other phenomena, gravitational sedimentation, Brownian movement, particle charging and evaporation and condensation are referred to, and a useful account of the recent work on the optical properties is given.

The problem of coagulation of particles is discussed in relation to a number of important situations and the effects of charging and of an acoustic field are considered. In the chapter on Deposition and Filtration, the problem of simultaneous diffusion and sedimentation is studied on the basis of von Smoluchowski's equation and the solution put forward by C. N. Davies. Then the factors influencing deposition during flow through channels and separation of the particles in a cyclone separator are considered. This is followed by a treatment of the flow round obstacles and its application to the separation of particles by filtration. The various snags which

are commonly met in sampling and in the subsequent size analysis of the particles are fully explained, and the use of the cascade impactor for effecting an initial separation into size fractions is described. The first section concludes with a chapter diffusion in the atmosphere, and the effects of climatic conditions discussed.

The second part, on industrial applications, is less comprehensive than the first. The first chapter is about the collection of the particles from an aerosol and includes the standard methods. It is odd that the reference to the Calder-Fox scrubber should be to *British Abstracts*, rather than to the original paper in the *Transactions* of the Institution of Chemical Engineers. Health hazards in various industries are mentioned, and there is a very inadequate account of the important question of flame propagation through dusts and mists. A matter of topical interest is that of atmospheric pollution which is taken next, and the book concludes with two chapters on natural aerosols and the uses of particulate clouds.

The book is well produced, though the relegation of the plates to the end is an irritating feature.

J. F. RICHARDSON

LA PROPULSION PAR FUSEES
(Rocket Propulsion)

M. BARRÈRE, A. JAUMOTTE, B. FRAEIJS DE VEUBEKE, and J. VANDENKERCKHOVE. Paris: Dunod, 1957. *ix* + 389 *pp.* (222 *illus.*)

THIS French publication, a joint production by four distinguished French and Belgian engineers, presents an excellent survey of the whole field of present day rocket work. Written before the launching of the first earth satellite, it suffers in no way from the Russian achievement—the possibility is there, to be read by all.

A very good feature is provided by Chapter I, which presents modern equipment, with photographs, in contrast to so many books on this subject which revert to the pioneer work with most indifferent fuels. This book is up-to-date—as far as any book can be in view of the rapid advances being made, and the military secrecy attempted.

Chapter I whets the appetite of the reader. By Chapter VII he has been led through broad principles, mathematical, it is true, but none-the-less presented very digestibly, to a thorough study of both solid and liquid fuel rockets. Several worked examples are included to supplement the theory, though it must be remarked that it is rare for the real life rocket designer to have such comprehensive and detailed data.

Chapter VII, Experimental Techniques in Rocket Propulsion, deals only with liquid fuel rockets. For solid fuel rockets many of the measurements required are of the same nature, but others are needed also. The techniques can differ. Incidentally, it is not understood why (page 218) in the case of a vertical test-bed it should be considered essential to deflect the jet.

There follow two valuable chapters on instabilities of combustion. Experimental difficulties encountered are analysed, and where possible theoretical explanations are given, with suggestions for the avoidance of the troubles.

The last three chapters, under the general heading of External Ballistics, unfortunately do not present such a full and comprehensive picture. Some aspects are treated fully; here for example is a good treatment of the problem of successive stage weights in a multi-stage missile. Chapter XI on Guidance is most curiously restricted to only two types of course, each of which is, however, investigated extremely thoroughly on the basis of a kinematical treatment. Chapter XII, being applications of the calculus of variations to the problems of optimum trajectories in the sense of minimum fuel consumption, will not seriously interest the practical rocket engineer.

In general, the book is most attractively written, profusely illustrated with photographs and drawings, with very clear and well-spaced typescript. There is a refreshing absence—so far as this reviewer can detect—of misprints. Occasionally the multiplicity of authors is betrayed by a change of symbols standing for the same quantity. Thus the effective exit velocity V_{ts} changes to c in the last chapter. There is also a most unwisely chosen symbol I_u introduced on page 202, and called 'l'indice de performance'. It is used there as the velocity increment for a given mass ratio rocket. There is grave danger of its being confused with the more usual performance index, or specific impulse, and indeed, in the preliminary table of notations I_u is not defined, while I (total impulse) and I_s (specific impulse) are.

In brief, an excellent book, with something of value for all workers in this field who can read French.

S. D. C. MUNDAY

THERMODYNAMICS FOR CHEMICAL ENGINEERS

H. C. WEBER and H. P. MEISSNER. 2nd ed. New York: Wiley; London: Chapman and Hall, 1957. *vi* + 507 *pp.* 68*s.*

THIS is an elementary textbook on thermodynamics for students of chemical engineering. The basic introduction to the subject is given in the first 175 pages: this covers the first and second laws, the entropy and other thermodynamic functions and also a chapter on perfect gases. There follow 25 pages on the theory of fluid flow, dealing with both compressible and incompressible fluids in the steady state. Thereafter come 32 pages of applications of fluid flow, covering the usual chemical engineering aspects, namely flow in ducts, with and without friction, changes in section and elevation, measurement of flow rates, etc. At the end of the book there are 181 pages on what is more strictly chemical thermodynamics, in which are given good accounts of chemical equilibria, phase equilibria, and finally a short section on electrochemistry.

All the above sections of the book appear to be soundly and clearly written, and to be well suited to those wishing to learn the subject. The treatment is throughout as descriptive as possible with, however, no concession to lack of rigour.

In the middle of the book there are three chapters on Power Cycles, Engines and Turbines, and Refrigeration. These are essentially descriptive: the absence of a more thorough discussion of the basic thermodynamic theory of power cycles is perhaps to be regretted.

Coming down to details some comment may be offered on the derivation of the flow equation

$$-v\,\mathrm{d}P=\mathbf{U}\,\mathrm{d}\mathbf{U}/g_c+\mathrm{d}F_R \quad . \quad . \quad . \quad . \quad (12.4)$$

on page 203. This equation can be derived either by

(*a*) considering a control volume (i.e. a volume *fixed in space*), and applying Euler's momentum theorem to it, or

(*b*) by equating the sum of the forces to the acceleration for an element of the *moving fluid*.

There appears to be some doubt in the author's account which method they are trying to follow.

Some protest must be registered against the use of the dimensional constant g_c, which appears repeatedly in the equations throughout the book: the use of this device appears to your reviewer to make confusion of thought doubly confounded, and to offer no advantage in either logic or simplicity.

Numerous problems are provided at the ends of the chapters: this is an innovation of this (second) edition.

R. F. STRICKLAND-CONSTABLE

Letters to the Editors

Letters to the Editors on points of scientific interest related to combustion and flames are invited. The Editors do not hold themselves responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Laminar Flame Theory

ALLOW me to draw your attention to a paper published by me in the *Canadian Journal of Chemistry* 34 (1956) 313 and whose result is similar to that obtained by D. B. SPALDING in his papers [*Combustion and Flame* 1 (1957) I—287 and II—296].

A formula for the flame velocity was derived in my paper which is identical to Spalding's formula 22 (page 292) if one lets

$$\lambda = \tfrac{1}{2}\,\tau_m^2$$

where τ_m is the value of τ corresponding to the maximum of the function $\phi(\tau)$. This gives exact values of V_u for the family (*vi*) of curves (page 302). For family (*i*), we find

$$\lambda = \tfrac{1}{2}[n/(n+1)]^2$$

which for practically important higher values of n differs very little from the value given by E. N. ADAMS

$$\lambda = \tfrac{1}{2}(n-1)/(n+1)$$

In most practical cases of combustion, $\phi(\tau)$ will be found to be somewhere between the curves (*i*) and (*vi*) so that the error in flame velocity obtained by my formula is of the order of 1 per cent only. The value τ_m is usually much easier to find than τ_c. It is felt, therefore, that in view of its great simplicity my formula will often be found useful.

R. SANDRI

Fuels and Lubricants Laboratory,
National Research Council,
Ottawa 2, Canada

(Received December 1957)

I AM grateful to Dr SANDRI for drawing attention to his paper, which was new to me. The line of thought is similar to that in my papers, having the following common features: (*a*) calculate flame-speed eigenvalues λ exactly for a family of reaction-rate expressions, (*b*) plot λ versus a simply determined characteristic of the reaction-rate functions, (*c*) assume that this plot of λ is also valid when the reaction-rate function does not belong to the assumed family.

His procedure differs in that: (*a*) the only exact solution he considers is that for the 'concentrated reaction' function, i.e. (*vi*) in my paper (page 302); (*b*) the characteristic of the reaction-rate function which he chooses is τ_m, the dimensionless temperature giving the maximum reaction rate. This contrasts with my choice of τ_c, the centroid of area beneath the reaction-rate curve. Since for his case $\tau_m = \tau_c$, his formula is identical with my equation 45 (page 302).

I agree that τ_m is more convenient, because more easy to evaluate, than the centroid position τ_c. I found, however, that plots of λ versus τ_m for the exact solutions were less successful in bringing points close to a single line than were plots of λ versus τ_c. I therefore chose the latter method of representation in my papers.

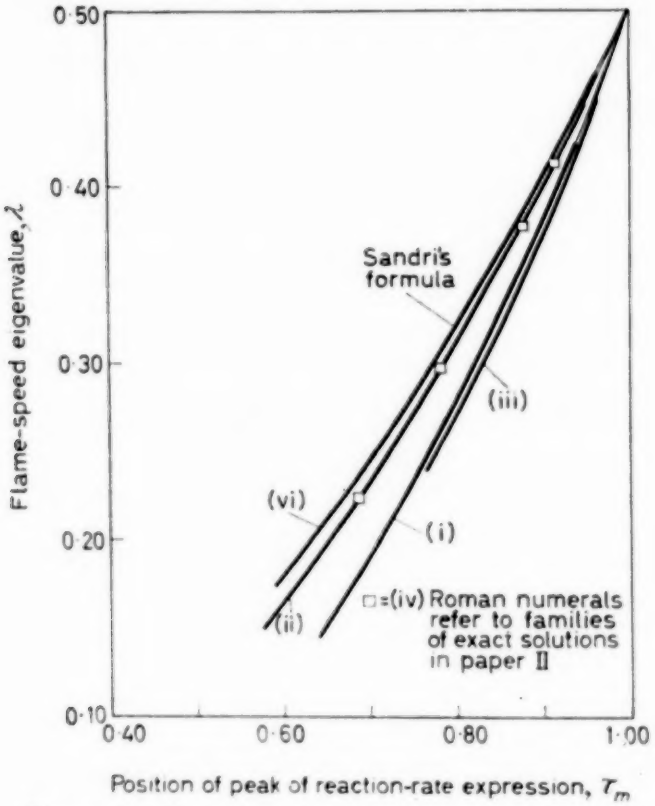

Figure 1. Exact λ values for several families of reaction-rate functions plotted versus τ_m

Figure 1 shows the way in which the different curves spread out when plotted versus τ_m. It should be compared with the exact solutions in my *Figure 4* (page 301). It appears that Sandri's formula [my solution (*vi*)] lies fairly close to the curve of family (*ii*) and the points of family (*iv*), which represent stoichiometric mixtures. The curves for families (*i*) and (*iii*), however, lie considerably lower over an important part of the range; these represent mixtures with an excess of one or the other reactant. To take as an example family (*iii*) at $\tau_m = 0{\cdot}8$, Sandri's formula would lead to an estimate of flame speed 8 per cent too low.

Of course 8 per cent is not much, and the advantages of a simple formula involving τ_m alone are considerable. If such a formula is desired, however, the graph shows it would be better to take, say,

$$\lambda = \tau_m - \tfrac{1}{2}$$

which is more accurate than Sandri's formula over the practical part of the range.

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Premixed Spherical Flames

A NEW type of burner has been developed for the study of premixed flames. It is a porous sintered ball, supported by a small quartz tube. Premixed gases are injected through the quartz support tube, and the flame stabilizes itself in spherical form around the ball. Flame gases are withdrawn from one or more points around the container with a suitable pumping system.

This new flame geometry provides three principal advantages:

(*1*) The spherical symmetry provides a unidimensional flame front* where there is a known relationship between gas density (or temperature) and gas velocity. By contrast, the gas velocity in ordinary bunsen flame fronts is an indeterminate function which must be measured separately from temperature[1].

(*2*) This flame minimizes the heat losses and material contamination which are severe at the edges of conventional bunsen burners[2]. This allows the production of unidimensional flames with low mass flows. Low pressure flames can thus be obtained with more modest pumping speeds than would be required for corresponding bunsen flames.

(*3*) Stable flames are produced over a wide flow range with a unidimensional flameholder whose effect can be measured and varied over a wide limit.

Such a system should be useful in the study of rich flames, the study of effects of initial temperature on flame propagation rate, and the study of flammability limits.

Several systems were used in preliminary tests: one utilized a 1 in. diameter sintered aluminium oxide sphere, and another a $\frac{1}{2}$ in. diameter porous sintered brass sphere. A 3 l. round-bottom flask was used for the outside container. Two different pumping systems were used—one a 5 l./s mechanical pump, and the other a $\frac{3}{4}$ l./s mechanical pump. With the latter pump, a plenum chamber was necessary to smooth out pumping fluctuations. Stable flames have been produced with methane–oxygen and propane–air mixtures. (Flames were burned at pressures from 6 to 300 mm

*In a unidimensional flame front composition, temperature and time are functions of a single distance parameter' which, in this case, is the radial distance from the centre.

of mercury and over a wide composition range.) The spherical symmetry, which was limited by the presence of the injection tube and the uniformity of the sintered material†, was good (see *Figure 1*).

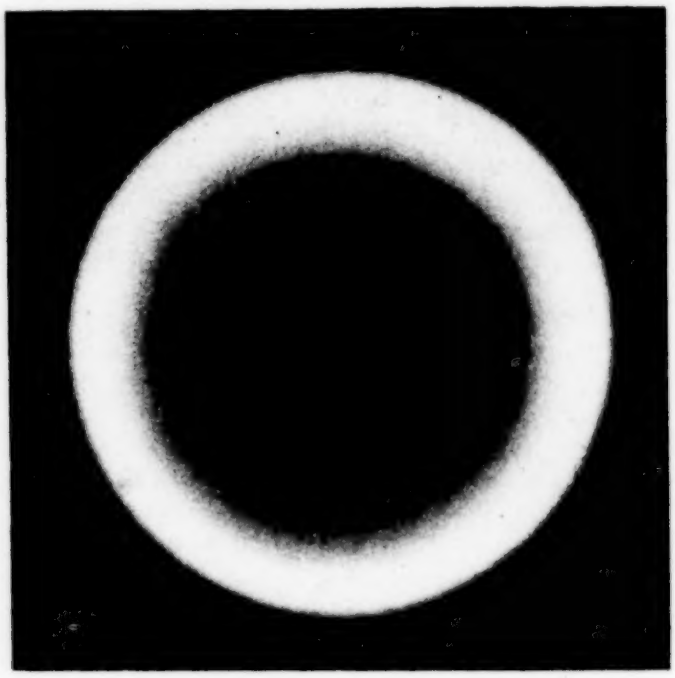

Figure 1. Premixed spherical flame: 0·1 methane 0·9 oxygen. Pressure, 1·3 cm of mercury

At a given equivalence ratio and pressure the surface temperature of the sphere decreased with increased mass flow and the diameter of the luminous zone increased. In the present system, mass flow is limited primarily by the pumping system, although other limitations can also be important. In the limit of very high mass flow, the surface temperature of the sphere would be expected to approach the injection temperature of the gas. In the case of one methane–oxygen mixture, stable flames were obtained with mass flows that gave surface temperatures ranging from 120° C to 700° C.

The spherical flame is related to two other burner systems; the spherical diffusion flame[2] and the porous flat flame burner[1].

A detailed study of the characteristics of spherical flames is under way.

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†Convection effects were unimportant in the low pressure region of these studies.

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Inhibition of Methane–Air Flames by Gaseous Aluminium Chloride

RECENTLY, J. E. DOLAN and P. B. DEMPSTER[1, 2] have reported that dispersed aluminium chloride powder is an effective inhibitor of the spark ignition of methane–air mixtures. We have examined the effect of aluminium chloride vapour on the burning velocity of methane–air mixtures and have found that this material is an effective flame inhibitor in the gaseous state as well.

The burning velocities of methane–air–aluminium chloride mixtures have been measured at 200° C. At this temperature, aluminium chloride is a liquid having a vapour pressure of 2·64 atm, the vapour-phase molecules[3] having the formula Al_2Cl_6. In these experiments aluminium chloride has been contained in a closed glass vessel having a capillary tube of 0·0085 in. bore as its only exit. With the vessel in a thermostatted wax bath at 200° C, there is a pressure drop of 1·64 atm across the capillary. In this way, a steady reproducible delivery rate of aluminium chloride has been attained. This rate can be varied by varying the capillary length or the bath temperature. Methane–air–aluminium chloride vapour streams of known composition have thus been prepared by passing metered methane–air mixtures by the capillary outlet and thence to a burner. The burner in our case has been an aluminium tube, 0·509 in. i.d. and 25 in. long. This has been immersed, except for the tip, in an inorganic fused salt bath thermostatted at 200° C. Flame speeds have been measured by photographing the cones and determining their areas.

The results obtained in this work are shown in *Figure 1*. The burning velocities of methane–air mixtures at 200° C are in good agreement with the results of G. L. DUGGER[4]. The following remarks may be made about these data:

(*1*) Aluminium chloride vapour is an effective inhibitor of methane–air flames. For example, the addition of 0·55 ± 0·04 per cent aluminium chloride vapour has reduced the burning velocity of the mixture containing 10 per cent methane (the fastest burning mixture) from 80 cm/s to 56 cm/s, a factor of 30 per cent. F. H. GARNER *et al.*[5], in a study of the inhibition of propane–air flames, found that the addition of 0·5 per cent carbon tetrachloride reduced the maximum burning velocity by about 15 per cent. There is evidence[6, 7] that the inhibiting effect of a halogenated methane increases with increasing number of halogen atoms. On this basis, it might be expected that aluminium chloride vapour would be roughly 50 per cent more effective than carbon tetrachloride. The fact that the effectiveness

of aluminium chloride vapour is of the order expected from extrapolation of results from halogenated methanes suggests that in each case the halogenated substance inhibits the flame by somehow removing active species.

(2) The inhibiting effect of aluminium chloride vapour is greater for rich than for lean mixtures. This is evident from the shape of the curves. It may be speculated that this indicates greater chain lengths for the flame reactions in the rich mixtures, but we have no other evidence on this point.

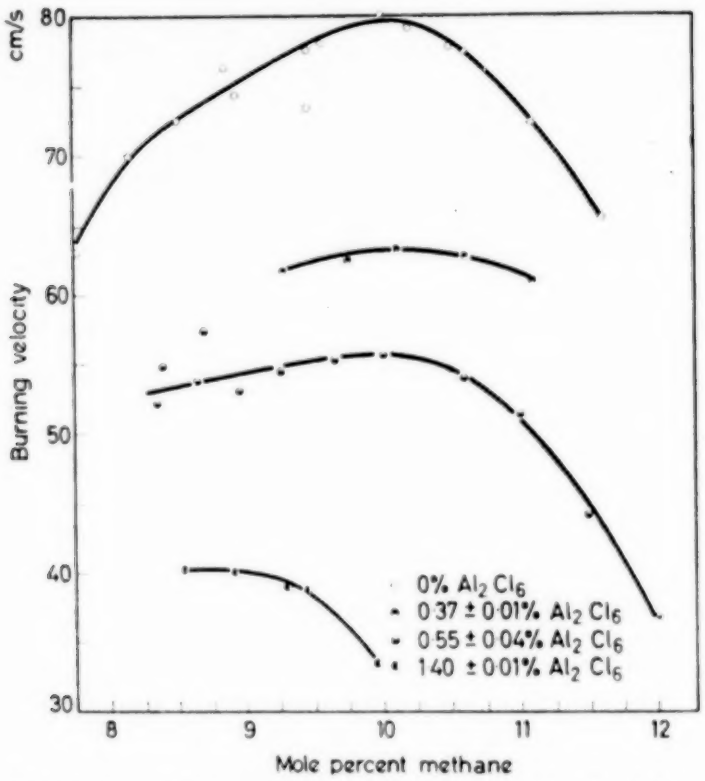

Figure 1. Burning velocity of methane–air–aluminium chloride mixtures at 200 °C

(3) Dolan and Dempster[1, 2] found that the addition of 0·63 per cent of aluminium chloride vapour prevented the propagation of the spark ignition into their 10 per cent methane–air mixtures*. We have found that methane–air–aluminium chloride vapour mixtures will burn stably with as much as 1·4 per cent aluminium chloride vapour present. We attribute this to the more favourable conditions for stable burning present in our burner as compared to their combustion tube and spark ignition source.

(4) The inhibiting effect of aluminium chloride vapour on methane–air flames is not linear with the inhibitor concentration. Thus for the 10·0 per cent methane mixture, 0·55 ± 0·04 per cent inhibitor reduces the burning velocity by 30 per cent. The addition of 1·4 per cent inhibitor effects a 58 per cent reduction rather than the 76 per cent called for by

The methane used by Dolan and Dempster[1, 2] contained 1·8 per cent ethane, 0·2 per cent carbon monoxide and 8·5 per cent nitrogen as impurities.

linearity. R. F. SIMMONS and H. G. WOLFHARD[6] observed a similar effect for ethylene–air–methyl bromide mixtures.

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Comments related to Flame Blowoff from Rectangular Burners

AN earlier publication[1] has stated that an anomaly exists in the treatment in reference 2 of the blowoff of flames from rectangular ports. J. GRUMER, M. E. HARRIS and H. SCHULTZ[2] correlated the stability of flames on non-circular and circular ports by means of the relationship

$$g = \lambda V R_e / 2\pi D^3 \qquad \ldots . [1]$$

where g is the actual boundary velocity gradient, V the actual volumetric flow, D the equivalent diameter = 4 times area/perimeter[3], and R_e the equivalent Reynolds number. The friction coefficient, λ, was obtained empirically by a procedure involving the value of D and is related to the Reynolds number. This treatment is limited by its composition to non-circular channels where the flow profile at the port for a particular volumetric flow and channel differs for the ignited and non-ignited streams. This consideration excludes slit ports where corner effects cannot be important.

N. R. L. MACCALLUM used equation 1 to predict the average gas velocities at blowoff from ports of 0·32 cm width and increasing length. Equation 1 should not have been used for all these ports because its use implies something that is unlikely—namely that the flow profile is different on slit ports for the ignited and non-ignited streams.

Apart from this consideration, the reported anomaly[1] resulted from the use of two values for the cross sectional area of the port[4]. This is not permissible, when equation 1 is used. Equation 1 uses the equivalent circular area $\pi D^2/4 = 4\pi(ab/a+b)^2$ to relate g and V. Maccallum used equation 1 to obtain V and converted V into an average gas velocity by

dividing the actual port area $4ab$ into it. Had the equivalent area been used to calculate the equivalent average gas velocity, no anomaly would have resulted. The evidence in reference 2 clearly shows that flames on non-circular ports can modify the approach flow profile. Equation 1 is only applicable to non-circular ports when this modification occurs. Then, if an average gas velocity is wanted, it must be the equivalent average gas velocity.

It is also noted that the flame-stability data for methane–air mixtures in reference 2 are not correlated by Maccallum's equation[1]. This is to be expected because these equations ignore the change in flow profile which was experimentally shown to occur[2] when the stream was ignited. The stability data for butane–air mixtures in reference 1 are not correlated by the equations of Grumer and his colleagues. Further study of the stability limits of flames on non-circular ports is needed.

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ALTHOUGH V, used by Grumer, Harris and Schultz in the equation $g=\kappa V R_e/2\kappa D^3$, correlating the results of stability determinations on circular and non-circular ports is the 'actual volumetric flow', it is evident from the letter of Grumer and Harris that it only belongs as such to the correlation. Grumer and Harris hold that, when applied to rectangular ports, the quantity V cannot be divided by the actual area of the rectangular port to give the actual average velocity. They consider that this is due to the flow profile being different for ignited and non-ignited streams: that may be, but it also shows up the need for a satisfactory theory in which quantities will have their real meaning, and not only a meaning which satisfies a use restricted to a particular equation devised for purposes of correlation. Dr Grumer's clarification of the use of his equation is welcomed, for it can be misleading unless its limitations are understood.

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